INDUSTRIAL
AND ENGINEERING
CHEMISTRY

Harrison E. Howe, Editor

EDITORIALS

SAFETY. The record shows that progress in safety is made only through tragedies and sacrifice. We are always locking the barn after the horse is stolen. The only comforting thought is that we do take some steps to prevent further stealing.

Those who work in laboratories where there is a constant hazard grow accustomed to the dangers peculiar to such places, just as the taxi driver becomes seemingly indifferent to all threats of tangled traffic. A periodic check of suitable facilities to meet emergencies threatening life should be made. There should be readily at hand all the effective means for extinguishing fires, for supplying first aid, and counteracting the effect of poisonous substances commonly used in the place. Of what value is a frozen emergency shower, an empty fire extinguisher, leaky hose, or an empty bracket designed to hold a blanket, so useful in smothering fires? It is difficult to remember all the factors involved in creating either a laboratory or a plant hazard, but there is no excuse for not having ready for instant use those appliances and measures known to be efficient, should an accident occur. We have reason to be proud of the safety record made in chemical plants, but the laboratory is in danger of being overlooked in safety programs.

IDENTITY BY SOURCE. On August 22, 1935, *H. R. 9185*, an omnibus liquor bill, was passed by the House of Representatives and since has been the subject of hearings before a subcommittee of the Senate Finance Committee. Senator Murphy of Iowa, on February 4, submitted an amendment which undertakes to define ethyl alcohol for the purposes of the Federal Alcohol Administration Act, the Food and Drugs Act, as amended, and any act of Congress amendatory or in substitution for either of said acts, according to its source. If it is enacted into law, no product could be labeled, advertised, or designated as neutral spirits, whisky, or gin, or any type thereof for nonindustrial use, if the neutral spirits contained therein were produced from materials other than grain. Under the amendment the term "neutral spirits" includes ethyl alcohol.

Straight whisky is all made from grain mash and the neutral spirits mentioned involve only about two million gallons annually used for blending purposes. But this amendment reaches over into the wide field of foods and drugs and if the idea prevails there are a number of other products in the still greater industrial markets that may soon be affected.

This is not the first time that efforts have been made to restrict by law the use of alcohol for legal beverage purposes to that derived wholly from grain or grain products. Chemists know ethyl alcohol to be a definite chemical compound, regardless of the raw materials from which it may be made, and there is ample evidence that the source of the materials used in the manufacture has no bearing on the purity of the final product. Indeed, there is no purer ethyl alcohol than that now made on a large scale from ethylene, and who can identify the source once pure alcohol is made? But if this type of legislation is to become law, what is to happen to the proposal to broaden the industrial use for other agricultural products? Only last year the United States Department of Agriculture issued a release in which it was proposed to use surplus potatoes for the production of alcohol. The molasses now used in most of the plants is a product of agriculture, whether cane or sugar beets, and there are plans under discussion for adding artichokes to the list as a raw material for alcohol. Wood may soon assume new importance in this connection.

Surely such discrimination will not be tolerated, even under the conditions of continual experiment which exist today. One might as well designate that the lead in the type metal to be used in printing the *Congressional Record* must be only that mined in the state of the senator proposing the resolution. And there are other absurd lengths to which we must go if any logic is to prevail. The whole idea is disgusting.

THE AIMS OF SCIENCE. Karl Compton, in his address as president of the American Association for the Advancement of Science, stressed among the aims of science the attack on still unconquered diseases, particularly the debilitating and disabling rather than the fatal, research in pure science as the spring board for forward leaps in application of science, the need for more intensified search for new outlets for agricultural products that there may be no need for crop limitations, and improvements in industrial processes.

Dr. Compton believes that tariffs, quotas, and other legislative measures amount to little more than coddling, which in the end handicap efficiency. To quote him:

> I believe that a second line of increased activity in applied science will occur in industry—particularly in those industries which have hitherto depended largely on tariff protection, on monopolies, on exploitation of natural resources, on governmental subsidies or simply on momentum of past strength. These supports are temporary and precarious; sooner or later they fall before science, because no amount of artificial protection can permanently maintain an obsolete product, an inferior process, or a moribund organization against competitors which are based on scientifically improved products or methods.

That there has been a decided reliance upon science by the most progressive of our industries is well illustrated by the statement of O. C. Huffman, president of the Continental Can Company. After discussing the substantial improvements in the plants of the company and in those built during the depression, Mr. Huffman concluded:

> It is not too much to say that the research and development work done during the depression may eventually appear as the means which led us out of it.

RIGHTING A MISTAKE. Perhaps the kindest thing to say is that the dairy lobby and others who were instrumental in securing the passage of the act which imposes three cents a pound tax on coconut oil simply failed to realize several fundamental errors in their course. The placement of this impost on a raw material largely imported from the Philippines was intended to increase our market for our own domestically produced fats and lead to their substitution for the oil from the Philippines in the manufacture of soap and in its use by tanners and the manufacturers of rubber articles. The money to be collected cannot go to the producer of the copra, but under the law must be paid into the Philippine treasury. The tax went into effect in 1934 and there is now before Congress the Guffey-Dockweiler Bill which is intended to remedy a situation now generally unsatisfactory.

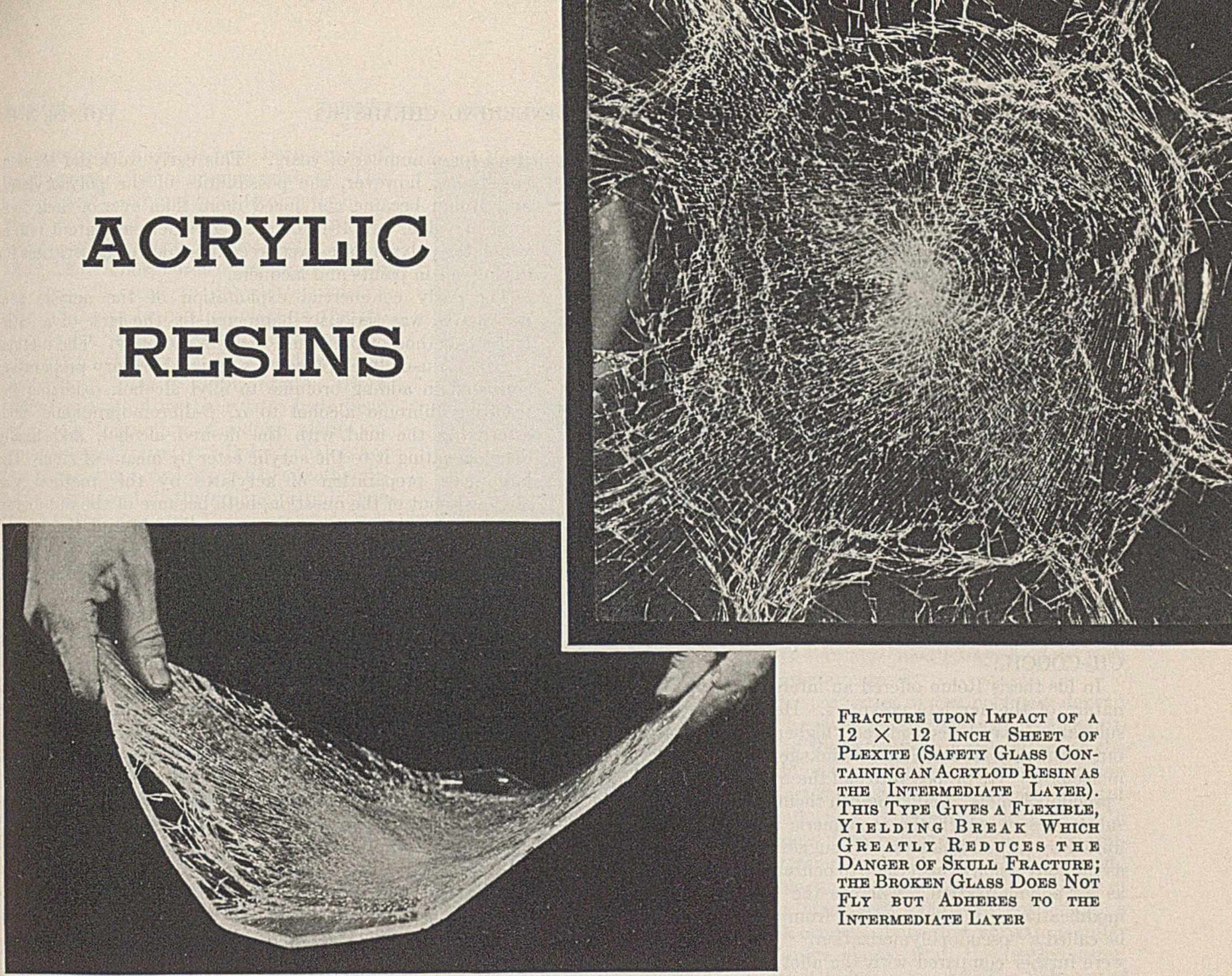
The imposition of the tax has worked a hardship on soap manufacturers who use coconut oil because of its lauric acid content, which is about 45 per cent. The production of some plants was on too small a scale to stand practically a 100 per cent increase in the cost of necessary raw material. Only large operators could manage that, even with the 36 per cent rise in the price of laundry soaps and 15 per cent for all varieties. Less soap was made and with the supply of coconut oil undiminished, the price with tax, while too high for soapmaking, was low enough in the world market to result in an increase in the proportion used for edible purposes. There were 284,000,000 pounds of refined coconut oil used for edible purposes in 1933, the year before the tax went into effect, and 364,000,000 pounds in 1935, the year following its imposition. Thus the dairy industry gained nothing as a result of the tax. The hardship to the producers of copra is unquestioned and so far no money has been paid into the Philippine treasury, for there are injunctions preventing this.

There are no domestic fats or oils that compete with coconut and palm kernel oils, because they alone contain lauric acid. As this lauric acid is what is required in the manufacture of zinc laurate, used as an accelerator in the rubber industry, is the compound which retards the yellowing of white kid, and produces the desirable lather in soap, it is obvious that these qualities are not obtainable with other fats and oils. Coconut oil, therefore, instead of competing with tallow and other inedible fats, actually increases their market, for they, too, are also desirable in various kinds of manufacture.

The Guffey-Dockweiler Bill proposes to retain the three cents per pound tax on that part of the importation used for edible purposes, to remove the tax where inedible uses are involved, and to denature that proportion, about 70 per cent of the imports, so that no difficulties can arise through illegal diversion. The bill refers to coconut oil produced in the Philippine Islands or in possessions of the United States, and statistics show that our industries can absorb practically the entire exportable surplus of this oil and copra produced in the Philippines.

There is a reciprocal side to the problem, for in 1926 the Philippines took $6,000,000 worth of our chemical products and even in the depression year of 1934 about $3,785,000 worth. By taking under favorable circumstances the products of the Philippines, the latter will be in better position to purchase from us, so that there is a beneficial economy involved, as well as righting an error evidently based on the assumption that oils and fats can be substituted one for another regardless of their chemical composition. As a matter of fact they are no more subject to interchange for special uses than are solvents, metals, or other products of unique characteristics.

ACRYLIC RESINS



Fracture upon Impact of a 12 × 12 Inch Sheet of Plexite (Safety Glass Containing an Acryloid Resin as the Intermediate Layer). This Type Gives a Flexible, Yielding Break Which Greatly Reduces the Danger of Skull Fracture; the Broken Glass Does Not Fly but Adheres to the Intermediate Layer

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ONE of the outstanding chemical developments of recent years in the industrial field is the rapid rise of synthetic resins to a position of considerable importance. Among the more recent of the commercially available resins are the polymers of the acrylic acid derivatives, known commercially as Acryloids.[1] Their commercial exploitation is another interesting example of the rather belated realization of the importance and value of substances known for many years. The credit for the recognition and industrial development of these substances belongs, in large measure, to Otto Röhm of Darmstadt, Germany, one of the early investigators in this field.

Historical Basis

Acrylic acid itself has been known for almost a hundred years. In 1843 Redtenbacher (*19*) reported the preparation of a new acid by the oxidation of acrolein with air and named it acrylic acid. The silver, sodium, and barium salts of this new acid were prepared by him. On the basis of later work (*8*) it appears likely that he also prepared the ethyl ester in an impure form. A solid modification (polymer) of acrylic acid, which gradually swelled in water and alcohol and "finally dissolved to a rubber-like acid" and formed salts with metals, was described by Linnemann in 1872 (*15*). In 1873 Caspary and Tollens (*7*) prepared the methyl, ethyl, and allyl esters and observed that the allyl ester polymerized at ordinary temperatures, especially in the sunlight, to give a "clear hard transparent mass." The polymer of methyl acrylate was first described by Kahlbaum in 1880 (*14*). The perfect transparency of the polymer and its remarkable physical properties led him to investigate it further. He established that its empirical formula was the same as that for methyl acrylate, and determined the solubility, specific gravity, and refractive index of methyl acrylate, its polymer, and a liquid product obtained by destructive distillation of the polymer in vacuum. Weger (*40*) reported the preparation of the methyl, ethyl, and propyl esters of acrylic acid in 1883, and commented on his ability to obtain only a limited amount of polymer from the methyl ester after long storage or persistent heating. The ethyl and propyl esters polymerized readily, and he described the ethyl ester polymer as being indistinguishable in appearance from the polymer obtainable from styrene. The preparation of acrylic acid chloride, anhydride, amide, and nitrile was described by Moureu in 1893 (*16*). He observed that the amide and anhydride polymerized readily.

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[1] For the sake of simplicity the term Acryloids has been applied to the various resins made from derivatives of acrylic acid, $CH_2{:}CH{\cdot}COOH$, and methacrylic acid, $CH_2{:}\underset{CH_3}{C}{\cdot}COOH$. They are manufactured and sold in this country by Röhm & Haas Company, Philadelphia. The trade name Acryloid is registered in the U. S. Patent Office.

In 1901 Röhm published the results of his researches with von Pechmann on acrylic acid derivatives (*18, 20, 23*). Röhm subjected methyl and ethyl acrylates to the action of sodium alcoholate in ether and isolated from the reaction mixtures a dimeric form, subsequently identified as the ester of α-methylene glutaric acid, and a trimeric form which was not further identified. In every case a considerable amount of solid polymer was formed, the methyl ester appearing to polymerize more readily than the ethyl ester. Röhm described the methyl acrylate polymer (*23*) as a colorless, transparent, very elastic mass practically free from any odor of monomer; insoluble in water, alcohol, and ligroin; but swelling in acetic acid, phenol, chloroform, acetoacetic ester, acetic anhydride, ethyl benzoate, and nitrobenzene. Boiling ether swelled the mass to six to eight times its volume and dissolved a small portion. Cold mineral acids had little action on the polymer, which was likewise resistant to the action of aqueous acid or alkali. Destructive distillation in vacuum gave a liquid distillate which was shown to contain α-methylene glutarate and a trimeric form, not identical with that obtained by the action of sodium alcoholate on methyl acrylate. Its structure appeared to be $COOCH_3{\cdot}CH : CH{\cdot}CH_2{\cdot}CH(COOCH_3){\cdot}CH_2{\cdot}CH_2{\cdot}COOCH_3$.

In his thesis Röhm offered an interesting comment on the nature of the acrylate polymers. He suggested that these substances may be considered "higher molecular compounds but without assuming a carbon linkage between the individual molecules." He proposed to call these and similar substances "pseudopolymers" to distinguish them from higher molecular substances in which the monomeric molecules are directly united by carbon linkages. He suggested that reactions such as the conversion of acetylene to benzene should be designated as a "polymerization," whereas the formation of the solid modification of methyl acrylate from the liquid form should be called a "pseudopolymerization." These pseudopolymers were further compared with the allotropic forms of the elements, such as phosphorus, sulfur, arsenic. It was suggested that rosin, rubber, and gutta-percha also belong to this class of substances. These comments are interesting as an example of one of the earliest speculations concerning the nature of these polymeric substances.

The most exhaustive recently published investigation into the nature of the polyacrylates appears to be that of Staudinger and his co-workers (*34, 35, 36*). There can be little doubt but that the polyacrylates, in common with polymers of other compounds containing a vinyl group, are composed of single molecules of high molecular weight, and that the monomeric units are joined by direct carbon-to-carbon linkages.

Industrial Development

The remarkable properties of the polymerized acrylates made a lasting impression on Röhm's mind. During the early part of his industrial career, the pressure of other duties prevented him from taking active steps toward any extensive commercial exploitation of the acrylate field. However, in the laboratory he worked indefatigably on a study of the many interesting properties of the polymers, and he was always on the lookout for possible uses for them. Eventually in 1912 he secured a German patent (*21*) in which it was claimed that by their vulcanization with sulfur the polyacrylates could be used as rubber substitutes. In the same year, work on the preparation of acrylic acid esters was started as part of a general program of investigation in the field of artificial resins. The war interrupted this work in 1914, and an opportunity for its resumption did not present itself for a number of years. This early work did serve to emphasize, however, the possibilities of the polyacrylates, and Röhm became convinced more than ever of their commercial value. In 1915 he secured a German patent (*22*) in which the polyacrylates were recommended as substitutes for drying oils in paints and lacquers.

The early commercial exploitation of the acrylic acid derivatives was seriously hampered by the lack of a satisfactory method of preparing them in quantity. The method (*7, 20, 37*) usually employed for their laboratory preparation consisted in adding bromine to allyl alcohol, oxidizing the resulting dibromo alcohol to α, β-dibromopropionic acid, esterifying the acid with the desired alcohol, and finally dehalogenating it to the acrylic ester by means of zinc. The large-scale preparation of acrylates by this method was obviously out of the question, both because of the number of reactions involved with a low over-all yield and the cost of the raw materials. Consequently, the discovery of a cheap and convenient method of preparing acrylates in quantity represented an important step in the development of this field.

The rapid development of chemical warfare and the manufacture of large quantities of mustard gas during the war emphasized the importance of ethylene as a raw material for the synthesis of many aliphatic substances. An ethylene derivative became the starting point of a new synthesis of acrylic acid esters, which made possible their manufacture on a large scale. This synthesis was worked out by Bauer (*30, 31*) in Röhm's laboratory, and by 1927 the work had progressed to the point where plant production of a limited quantity of methyl acrylate could be commenced. The synthesis is based on the use of ethylene chlorohydrin as a starting material and is effected in essentially two major operations, although a number of reactions are involved in the second operation. The reactions involved are as follows:

$$CH_2OH{\cdot}CH_2Cl + NaCN \longrightarrow CH_2OH{\cdot}CH_2CN + NaCl \quad (1)$$

$$CH_2OH{\cdot}CH_2CN + ROH + H_2SO_4 \longrightarrow CH_2{:}CH{\cdot}COOR + NH_4HSO_4 \quad (2)$$

In 1931 the production of acrylic esters was begun in this country by the Röhm & Haas Company. The methods of operation were based on the synthesis discovered by Bauer but were modified considerably in many details in order to increase their efficiency.

This method is best suited for the production of the esters of the lower alcohols. For the manufacture of the acrylates of the higher alcohols it is sometimes preferable to resort to direct esterification of the acrylic acid or to a transesterification between a lower acrylate and the higher alcohol. The acrylates can also be prepared from acrylyl chloride and alcohol (*5*), or by the catalytic dehydration of hydracrylic esters (*2*).

The ease and violence with which the acrylates can polymerize make it generally undesirable either to store or transport them in the monomeric form. The addition of polymerization inhibitors increases their stability but cannot be relied upon always.

Homologs of the Acrylates

Of the homologs of acrylic acid esters, the beta-substituted ones polymerize slowly, if at all, and consequently are of little interest as a source of polymeric materials. Although esters of the alpha homologs have been known for many years (*6*), only those of the methyl homolog can be prepared with sufficient ease to be of commercial interest. Ethyl α-methylacrylate seems to have been prepared for the first time by Frankland and Duppa in 1865 (*10*). Some years later its tendency to polymerize was commented upon by Fittig and Paul (*9*).

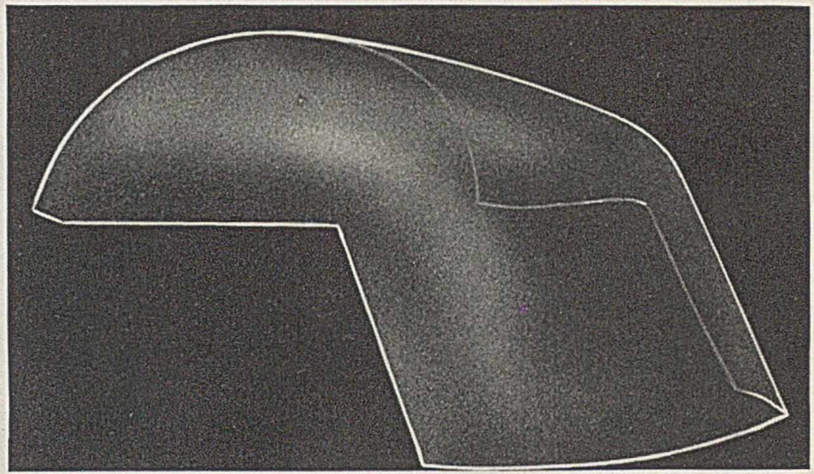
A number of methods have been reported for the preparation of methacrylates.[2] The method first used and most frequently mentioned is that of treating an α-hydroxyisobutyric acid ester with phosphorus trichloride (*9, 10, 33*). Phosphorus oxychloride, which has been observed to dehydrate hydroxy esters (*38*), can be used in place of the trichloride to give good yields of the methacrylate. Thionyl chloride likewise dehydrates the hydroxy ester to methacrylate. Both methyl and ethyl methacrylates have been formed by the action of sodium nitrite on α-aminoisobutyrate (*1*). Dehydrohalogenation of an α-bromoisobutyrate to a methacrylate by means of diethylaniline or quinoline (*11, 12, 39*) has also been recommended. β-Chloroisobutyric esters are readily dehydrohalogenated by means of basic ferric chloride or alcoholic caustic (*26*). Esters of α-hydroxyisobutyric acid are easily and economically prepared from acetone cyanohydrin. For this reason they are convenient starting materials for the manufacture of various methacrylic acid esters. The manufacture of methacrylates in quantity offers no particular difficulties other than the avoidance of loss through polymerization. Similar to the acrylates, the monomeric methacrylates cannot be stored or transported with safety.

Polymerization and Polymeric Forms

The esters of both acrylic and methacrylic acids polymerize readily under the influence of heat, light, oxygen, and oxygen-yielding substances such as sodium peroxide, hydrogen peroxide, and benzoyl peroxide (*25*). In general, the acrylates polymerize much faster and therefore more violently than the corresponding methacrylates. For this reason the polymerization of large quantities of acrylates must always be done with the greater care.

The properties of the polymers depend to a large degree on the chemical constitution of the monomeric forms, although the conditions under which the polymerization is effected also have a considerable amount of influence. Polymethyl acrylate is a colorless, transparent substance. At ordinary temperatures a film of it is tough, pliable, and so elastic as to be capable of being stretched 1000 per cent before a break occurs. Polyethyl acrylate is softer and more elastic than the methyl ester, and not quite so tough. The polymer of *n*-butyl acrylate is so soft that at ordinary temperatures it sometimes becomes rather sticky to the touch. In general, the softness of the polymers increases regularly as the length of the alcohol chains increases. For example, the polymers of octyl and lauryl acrylates are so soft as to be classed as semi-liquids.

As might be expected, isomeric variations within the alcohol group have a marked influence on the characteristics of the polymer. The polymer of isobutyl acrylate is noticeably harder and tougher than that of the *n*-butyl ester, being similar in its physical properties to the *n*-propyl acrylate polymer. The secondary butyl acrylate polymer is still harder, approaching the properties of the methyl ester polymer in this respect. Although the polymeric *n*-butyl, isobutyl, and *sec*-butyl acrylates vary in their degree of softness, all of them are elastic and pliable. In the case of the *tert*-butyl acrylate the polymer has lost practically all of



TOP: ACRYLOID HOOD FOR A PASSENGER PLANE, FORMED OF ONE PIECE AND BENT ON THREE SIDES, PERMITTING AN UNIMPAIRED VIEW

CENTER: VIOLIN MADE FROM ACRYLOID

BOTTOM: GROUP OF OBJECTS MADE FROM ACRYLOID

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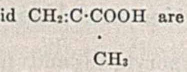
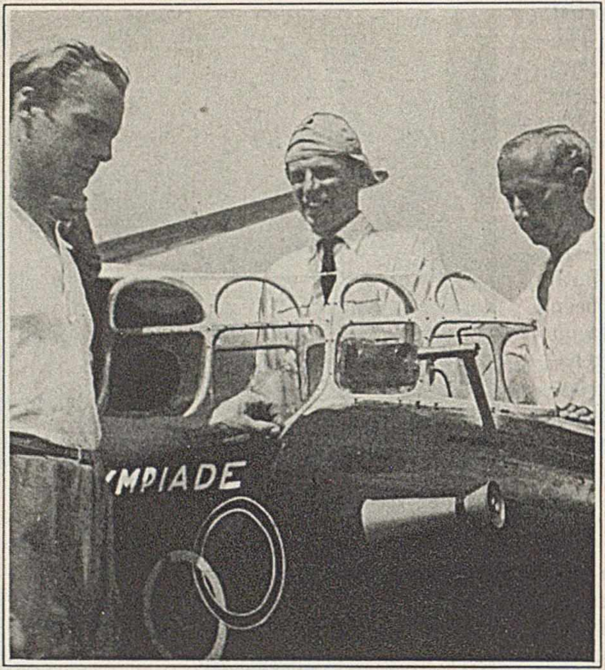
[2] Esters of the acid

$CH_2{:}\underset{CH_3}{C}{\cdot}COOH$ are referred to hereafter as "methacrylates" rather than "α-methyl acrylates" in order to avoid their confusion with methyl acrylate, the methyl ester of acrylic acid.



Racing Car Equipped with Acryloid Windows

its pliability and is a hard, tough solid, almost brittle at ordinary temperatures. The *tert*-butyl acrylate polymer seems to be the hardest of all the aliphatic acrylate polymers. The relationship between the various isomeric polyamyl acrylates is the same as that of the butyl esters, except that the corresponding polymer in each case is slightly softer. A carbon ring increases decidedly the hardness of the polymer. The polymer of cyclohexyl acrylate is quite hard and tough, whereas the *n*-hexyl ester polymer is soft and tacky. Ethylene glycol diacrylate polymer is extremely hard and practically insoluble in organic solvents.

The general influence of variations in the structure of the alcohol group is the same for the polymethacrylates as for the polyacrylates. However, as a class, the polymethacrylates are considerably harder than the polyacrylates. Whereas polymethyl acrylate is a rather soft, elastic, rubber-like substance, polymethyl methacrylate is a very hard, tough mass which can be sawed, carved, or worked on a lathe with ease. It is only when the *n*-amyl ester is reached that the softness and pliability of the polymer approach those of polymethyl acrylate. The higher homologs of acrylic acid, such as ethacrylic and propacrylic acid, are difficult and expensive to prepare, and their esters polymerize extremely slowly to give soft, semi-liquid polymers.

By modifying the conditions under which polymerization is caused to take place, it is possible to obtain from the same monomeric ester, polymers which vary from quite tough, almost insoluble forms to elastic, rather soft, tacky, and highly soluble varieties. The viscosity of a given polymer may be influenced at will by changes in the catalyst, the solvent, and the temperature used during polymerization. The presence of impurities has also been shown to have a definite influence on the properties.[3] In general, mixtures of different polymers do not show the desirable properties to be expected. However, this difficulty may be entirely overcome and additional advantages obtained when the monomeric forms are mixed in desirable proportions before polymerization is effected (*17*).

Both acrylic and methacrylic acids are polymerized by much the same agents as are used for the polymerization of the esters. The polyacids can be obtained either as hard, rather brittle, transparent, colorless masses or as white powders. Polyacrylic acid gradually swells and dissolves in water to give highly viscous solutions which are useful as thickeners for emulsions, as are also the solutions of the alkali salts of the polyacid. Acrylonitrile (vinyl cyanide) and methacrylonitrile polymerize rather slowly to give white powders, insoluble in practically all common organic solvents. The nitriles are useful, chiefly as components of joint polymers with acrylates or other polymerizable compounds.

Because of the considerable influence of the conditions of polymerization on the character of the polymer and of the violence with which the polymerization can sometimes take place, the polymerization of large quantities of acrylates and methacrylates must be carried out under carefully controlled conditions. With the exception of the lower esters of methacrylic acid, the polymers find their greatest usefulness in the form of solutions in organic solvents or as aqueous emulsions. The solutions of the polymers in organic solvents are water-white and vary in viscosity from thin liquids to semi-solids, depending on the type and amount of polymer present. Emulsions of the polyacrylates (*13*) greatly resemble rubber latex in appearance and in many of their properties. In certain processes they can be substituted for rubber latex. Solid polymers in granular or powder form are obtained by polymerizing in a liquid which is a solvent for monomer but in which the polymer is insoluble (*28*).

Properties and Uses[4]

The polymers of the acrylates and methacrylates are capable of being produced in a wide variety of forms, but as a class they are distinguishable from other resins by their colorless transparency, adhesive qualities, great elasticity, and resistance to many reagents. The brilliant water-white color of the polymers makes it possible to secure masses of high light transmission and great optical clarity. Because of the remarkable stability of the polymers to the action of heat and light, these properties are permanent.

In regard to hardness, toughness, and elasticity, they range from the very hard, tough polymers of methyl methacrylate to the very soft, sticky semi-liquid polymers of the higher aliphatic acrylates. The water absorption varies from almost 0 up to 2 or 3 per cent, depending on the composition and type of polymer. As a class they have good electrical resistance. Polymethyl acrylate, for example, has a dielectric constant of 5–6, a surface resistivity at 1000 volts of $4–5 \times 10^6$ megohms, and a specific electrical resistance of 4×10^{12} ohms. The extensibility of the polyacrylates is generally greater than that of the polymethacrylates.

The polymers are generally insoluble in water, alcohols, and aliphatic hydrocarbons. Most of them are only slightly swelled by ethers. On the other hand, they are either completely dissolved or swelled to soft gels by coal-tar hydrocar-

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[3] Staudinger and Trommsdorff [*Ann.*, 502, 201–23 (1933)] give an interesting discussion of the influence of the degree of polymerization on the properties of polyethyl acrylate.

[4] Patent applications for a variety of uses have been made by Röhm & Haas Company, Philadelphia, and Röhm & Haas, A.-G., Darmstadt.

bons, chlorinated hydrocarbons, ketones, esters, ether alcohols, and ether esters. They show excellent resistance to dilute acids, and their resistance to dilute alkali is good. The lower methacrylate polymers appear to be quite resistant to hydrofluoric acid fumes. Both the polyacrylates and polymethacrylates are permanently thermoplastic.

The acrylate and methacrylate polymers are characterized by their excellent adhesion to most surfaces. In the case of metal surfaces, baking further improves the adhesion.

The properties described make the polyacrylates and polymethacrylates especially suitable for a variety of uses. One of the earliest practical uses for the polyacrylates was as an intermediate layer in laminated glass (*29*). Because of their optical clarity, stability to light and heat, toughness, and excellent adhesion, these polymers were particularly suited for this purpose. Furthermore, they can be readily applied directly to the glass sheets in the form of their solutions (*27*). However, the polyacrylates have the disadvantage, stated previously and common to most plastics used in laminated safety glass, of being influenced to a marked degree by temperature changes. This defect has been largely overcome by using a joint polymer made by polymerizing a mixture of several different monomeric forms (*17*). Laminated safety glass made from this type of polymer is being manufactured and sold in this country under the trade name of Plexite. In Europe laminated glass containing polyacrylic acid derivatives is known as Luglas and Sigla.

The electrical resistance of the polymers is sufficient to make them of value in electrical insulators. The polyacrylates are especially useful (*24*) where a pliable insulating medium is desired. In cases where tough, rigid insulators are required, the polymethacrylates, especially polymethyl methacrylate (*32*), are recommended. The adhesive nature of the polymers opens up a wide field of application (*3*). Their solutions in organic solvents are well suited for use in clear lacquers and varnishes, for coatings on metals, wood, paper, etc., and for undercoatings and finishes on textiles. Their resistance to mineral oils makes them useful as coatings for gasoline and lubricating oil storage tanks. By the proper choice of solvents they can be made suitable for application by either spraying or brushing. The water emulsions offer a convenient form for their application in certain types of problems—for example, as undercoatings in leather finishes. Their uses are increased by adding pigments and fillers. Their compatibility with other resins and cellulose derivatives varies considerably with different polymers and even with different types of the same kind of polymer. In general, the cellulose nitrates are compatible with more forms than are the cellulose acetates. The cellulose ethers are compatible in some cases.

Sheets, blocks, rods, and molded, sawed, or turned objects of methyl or ethyl methacrylate polymers are of a brilliantly clear, water-white transparency. Their hardness, toughness, and light weight (specific gravity 1.18) add to their attractiveness. These polymers readily lend themselves to use as substitutes for glass in optical lenses, high ultraviolet-light transmitting sheets, *objets d'art*. Many striking and beautiful effects can be produced by the incorporation of dyes and pigments. Large quantities of clear sheets of these polymers are being used in airplane windows in Europe.[5]

Chlorination of the polymers of the acrylic and methacrylic acid esters has a marked influence on their properties (*4*). For example, chlorinated polymethyl acrylate is insoluble in chloroform, ethyl acetate, and many other solvents in which it was soluble before chlorination. Chlorination also increases the hardness and raises the softening point of the polymers.

It is apparent from this discussion that the acrylic resins show many unique physical, chemical, and mechanical properties. In view of the practically inexhaustible supply of raw materials and the many and varied uses to which all of these products have been already put, there is every reason to believe that in the future we shall see a rapid increase in the number of fields in which the acrylic resins will be used to advantage.

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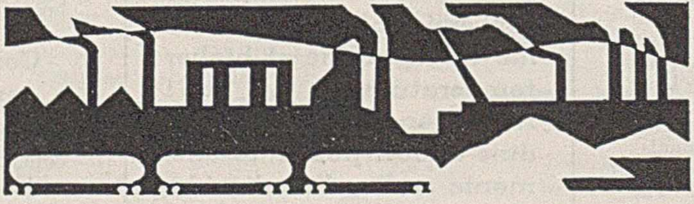

GUANIDINE FROM CYANAMIDE...

Preparation in Presence of Ammonium Phosphates

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A study was made of the preparation of guanidine from cyanamide and the ammonium phosphates. The maximum yield was obtained when a mixture of cyanamide and diammonium phosphate in the molar ratio $H_2CN_2:NH_3:H_3PO_4 = 1:2:1$ was autoclaved at 140° C. for one hour. Under these conditions a yield of 70 moles of guanidine per 100 moles of cyanamide was obtained. The remainder of the cyanamide was converted to urea and to ammonia in about equal amounts.

The course of the reaction appears to be the rapid formation of dicyanodiamide at an intermediate temperature followed by conversion of dicyanodiamide to guanidine at higher temperatures. At still higher temperatures guanidine decomposes to ammonia and carbon dioxide.

PREPARATION of guanidine represents one phase of an investigation of the conversion of calcium cyanamide into other compounds of nitrogen possibly more suitable for utilization in fertilizers. Free cyanamide exhibits three typical reactions, (1) polymerization to dicyanodiamide, (2) hydrolysis to urea, and (3) ammonolysis to guanidine—e. g.,

$$2H_2CN_2 = H_4C_2N_4 \qquad (1)$$

$$H_2CN_2 + H_2O = CO(NH_2)_2 \qquad (2)$$

$$H_2CN_2 + NH_3 = CH_5N_3 \qquad (3)$$

The availability of the nitrogen in dicyanodiamide and urea has been studied many times, but little is known concerning the use of guanidine salts for fertilizer purposes (*6*). Present indications are that they form stable mixtures with various fertilizer ingredients and are not toxic to plants. Tests comparing the availability of guanidine to growing plants with the common nitrogen carriers are now in progress in several state experiment stations. Certain properties of guanidine, such as high nitrogen content, strong basicity, and nonhygroscopicity of certain salts, were considered sufficiently valuable to warrant a study of a process for its preparation in the form of a salt. The phosphate was chosen for detailed study since this salt has good physical properties and contains two of the elements necessary for plant growth, nitrogen and phosphorus.

Experimental Procedure

APPARATUS. In the study of ammonolysis of cyanamide, use was made of a rocking autoclave. It was essentially a tee turned from a nickel steel forging, closed by blank flanges, and mounted on trunnions with the side branch up. Through the top flange on the side branch, connections were made to the interior of the autoclave for the ammonia line, pressure gage, blowdown valve, and thermometer well. The thermometer well, which extended almost to the opposite wall, was partly filled with lubricating oil to facilitate heat transfer from the charge to the mercury thermometer. An electrical heating element was embedded in insulation over the main branch. The total volume was 4.5 liters and the volume of the usual charge was about 2 liters. For following the course of the reaction, six small tool steel bombs, similar in design to the bomb for the Parr peroxide calorimeter, were used. The volume of each bomb was 20 cc. and the charge was held to half this volume.

CYANAMIDE SOLUTION. Concentrated stock cyanamide solutions were prepared by the procedure developed by Hetherington and Braham (*5*). One solution so prepared and used in most of the experiments to be described contained 43.7 per cent total nitrogen, 40.4 per cent cyanamide nitrogen, 0.6 per cent urea nitrogen, a trace of dicyanodiamide, and no guanylurea. Pure dicyanodiamide was prepared by recrystallization of dicyanodiamide formed by boiling a solution of cyanamide at the proper pH (*5*).

AMMONIUM PHOSPHATE. The monoammonium phosphate was a technical grade prepared in the laboratory. This material, analyzing 11.3 per cent nitrogen and 62.0 per cent P_2O_5, contained some free H_3PO_4. The desired ammonium phosphates were prepared in the autoclave as required by adding aqua or anhydrous ammonia to a charge of this monoammonium phosphate in a solution of cyanamide.

ANALYTICAL METHODS. Cyanamide was determined by the ammoniacal silver precipitation method (*7*). Dicyanodiamide was extracted with acetone, converted to guanylurea, and precipitated with nickel (*4*). Total nitrogen and ammonia nitrogen were estimated by A. O. A. C. methods (*1*). The Vorzarik ammoniacal picric acid method (*8*) was used to determine guanidine. Urea was estimated by the urease method (*3*).

EXPERIMENTS IN AUTOCLAVE. In order to determine optimum conditions for the preparation of guanidine phosphate from cyanamide, an experimental study of the reaction between cyanamide and ammonium phosphates was made to determine the effect of (1) concentration of cyanamide in solution, (2) mole ratio of ammonia to cyanamide, (3) mole ratio of phosphoric acid to ammonia, (4) temperature, and (5) time of heating.

Concentration of Cyanamide and Ammonia

Preliminary results indicated that considerable conversion of the cyanamide to guanidine occurred at 140° C.

in the presence of diammonium phosphate. Solutions containing 10, 20, 30, and 40 per cent by weight of cyanamide nitrogen were therefore mixed with varied proportions of monoammonium phosphate, and sufficient ammonia was added to give 2.2 moles of ammonia per mole of H_3PO_4. The data obtained by autoclaving these mixtures for one hour at 140° C. are shown in Figure 1. Over the range of ammonia concentrations investigated, maximum yields of guanidine were obtained from solutions containing 20 per cent cyanamide nitrogen. Ammonia in the proportion of 1.5 or 2.0 moles per mole of cyanamide produced better yields from all four concentrations of cyanamide than were obtained from the 1:1 mole ratio.

Ratio of Ammonia to H_3PO_4

The effect of varying the ammonia–phosphoric acid ratio on the yield of guanidine was studied next. In this study the autoclave charges were prepared by adding to the cyanamide solution (20 per cent nitrogen by weight) monoammonium phosphate and sufficient ammonia to vary the mole ratio of ammonia to H_3PO_4 from 6 to 1. In each case there were present in the charge 1.5 moles of ammonia for each mole of cyanamide. Each mixture was autoclaved for one hour at 140° C.

The results obtained for these conditions are shown in Figure 2. The maximum yield of guanidine was obtained from the use of 2.2 moles of ammonia per mole of H_3PO_4. When less than 2.2 moles of ammonia were present, the products from the autoclave contained considerable quantities of ammonium carbonate which increased as the acidity of the charge increased. With more than 2.2 moles of ammonia per mole of H_3PO_4 the yield of guanidine decreased. At the same time dicyanodiamide appeared in the products in amounts which corresponded to the decrease in guanidine. Since, as is shown later, dicyanodiamide is an intermediate product in the formation of guanidine, the yield of the latter could have been increased by changing conditions of autoclaving so as to ammonolyze the dicyanodiamide.[1]

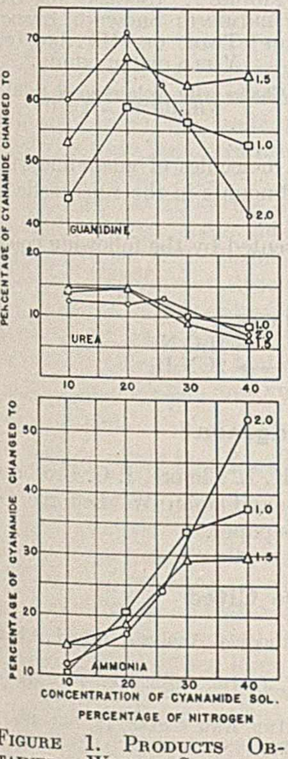

Figure 1. Products Obtained When Solutions Containing 10, 20, 30, and 40 Per Cent Cyanamide Nitrogen Were Heated with 1.0, 1.5, and 2.0 Moles of Ammonia per Mole of Cyanamide

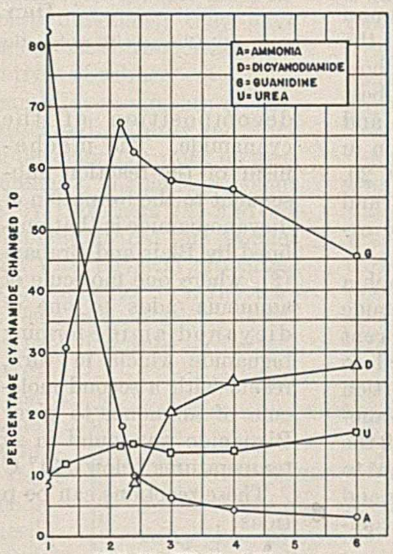

Figure 2. Effect of Changing Molar Ratio of Ammonia to H_3PO_4

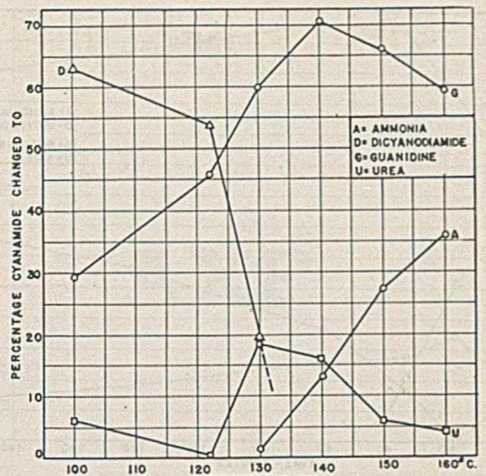

Figure 3. Effect of Temperature

Ratio, moles $H_3PO_4:NH_3:H_2CN_2$ = 1:2.2:1.1.

The amount of urea in the products showed only slight increase as the mole ratio of ammonia to H_3PO_4 was increased from 1 to 6.

Temperature and Time of Heating

Effect of temperature was determined by heating a mixture of cyanamide solution containing 20 per cent nitrogen with diammonium phosphate in the autoclave for one hour at 100°, 120°, 130°, 140°, 150°, and 160° C. Two moles of ammonia were used for each mole of nitrogen in the cyanamide solution. The maximum yield was obtained at 140° C. (Figure 3). A change in temperature of 10° above 140° caused more ammonia to be formed; at 10° below 140°, considerable dicyanodiamide remained in the product.

Charges of the same composition as were used for determining the effect of temperature were heated at 140° C. for different intervals of time varying from 3 to 180 minutes. The results are shown in Figure 4. The yield of guanidine increased with time up to one hour, after which a gradual decrease occurred due to decomposition of guanidine. Dicyanodiamide was present in mixtures heated a short time. The decrease in quantity of dicyanodiamide with increase in time corresponded to the increase in guanidine.

No attempt was made to identify the salts present in the product. However, the vapor pressure of the products where little ammonia was formed indicated the presence of diammonium and diguanidine phosphate. Both of these salts were isolated by fractional crystallization of the product from water. From those products in which large quantities of ammonia were formed, ammonium carbonate and ammonium carbamate sublimed and were deposited in the colder portion of the autoclave on cooling.

The product obtained by heating the cyanamide solution with diammonium phosphate under the optimum conditions for obtaining the maximum yield of guanidine contained also urea and ammonia, and was entirely free from dicyanodiamide and insoluble forms of nitrogen. The product offers promise as a fertilizer material.

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[1] A study of the preparation of guanidine from cyanamide and various ammonium salts in the presence of free ammonia is in progress.

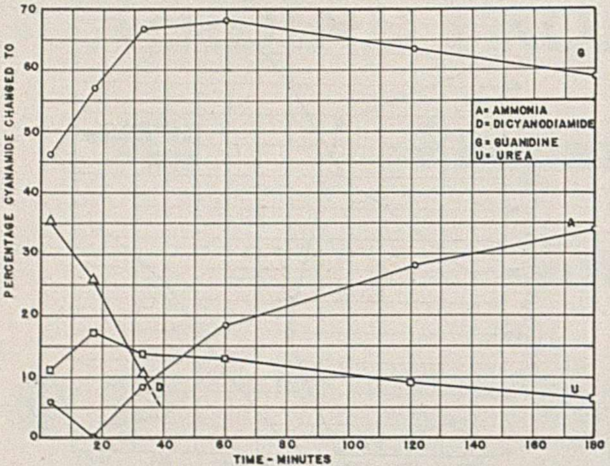

FIGURE 4. EFFECT OF TIME

Reaction Mechanism in Guanidine Formation

EXPERIMENTS IN SMALL BOMBS. The data obtained in the autoclave experiments are not adapted to interpretation of the mechanism of guanidine formation because of the various reactions which may occur during the 45 to 50 minutes required to raise the temperature of the charge to the optimum temperature of 140°. In order to ascertain the course of the conversion, solutions of cyanamide and diammonium phosphate in the proportions previously found to give the best yields of guanidine were placed in small steel bombs and brought rapidly to a temperature of 140° C. by immersion in a preheated oil bath. After heating for periods of 2, 10, 20, 40, 60, and 120 minutes, the bombs were withdrawn and chilled immediately in cold water. The results of these experiments are shown in Figure 5.

The charge heated for 2 minutes probably did not reach a temperature of 140° C. throughout; of the cyanamide charged, 11.0 per cent remained unchanged, 69 per cent formed dicyanodiamide, and 6 per cent was converted to guanidine. As the reaction period increased, the proportion of guanidine in the product increased and that of dicyanodiamide decreased. Probably dicyanodiamide represents the primary product which, in turn, undergoes conversion to guanidine. The decrease in the sum of dicyanodiamide and the guanidine percentages is indicative of further decomposition.

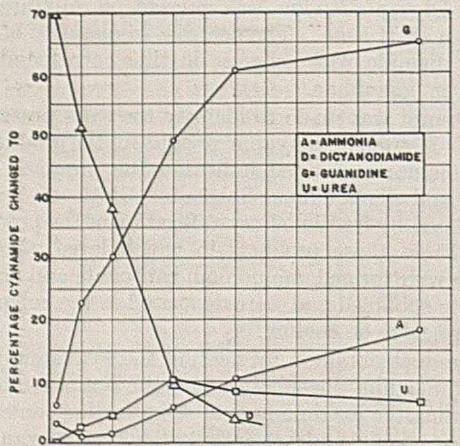

FIGURE 5. MECHANISM OF GUANIDINE FORMATION AS SHOWN BY DURATION OF HEATING SMALL-SCALE EXPERIMENTS

Ratio, moles $H_3PO_4:NH_3:H_2CN_2 = 1:2:1$.

In another series of one-hour runs at 140° C., the cyanamide in the charge was replaced partially or wholly by dicyanodiamide. The percentage yield of guanidine based on the sum of cyanamide and dicyanodiamide nitrogen decreased as the proportion of dicyanodiamide increased (Figure 6). With dicyanodiamide alone 1.5 hours were required at 140° to yield approximately the same amount of guanidine as given by cyanamide in one hour (Figure 7). This indicates that dicyanodiamide formed from cyanamide in the course of the reaction is more reactive than the dicyanodiamide charged in the form of crystals.

The yield of guanidine was less in the small bombs than in the autoclave, partly because of the greater rate of decomposition induced by the increase in proportion of bomb surface to volume of charge. Also the rate of heating the charge may change the rate of various reactions involved in the decomposition of the cyanamide. The mechanism of the reaction subsequent to the formation of dicyanodiamide is that outlined by Blair and Braham (2), where one molecule of ammonia adds to one of dicyanodiamide forming biguanide which, in turn, reacts with a second molecule of ammonia to give two molecules of guanidine salt. Biguanide was found in small amounts in the runs made at temperatures below 140° C.

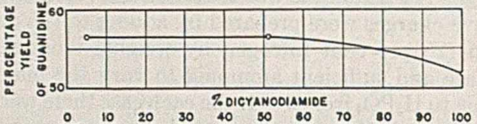

FIGURE 6. MECHANISM OF GUANIDINE FORMATION AS SHOWN BY SMALL-SCALE EXPERIMENTS USING A MIXTURE OF CYANAMIDE AND DICYANODIAMIDE

Charge with mole ratio of $H_3PO_4:NH_3:H_2CN_2 = 1:2:1$.

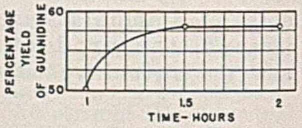

FIGURE 7. SMALL-SCALE EXPERIMENTS SHOWING EFFECT OF TIME OF HEATING ON YIELD OF GUANIDINE

Charge with mole ratio of $H_3PO_4:NH_3:H_2CN_2 = 1:2:1$

These reactions can be represented by the following equations:

$$2H_2CN_2 \longrightarrow H_4C_2N_4$$
$$H_4C_2N_4 + NH_3 \longrightarrow H_7C_2N_5$$
$$H_7C_2N_5 + NH_3 \longrightarrow 2CN_3H_5$$

Acknowledgment

The authors are indebted to K. L. Elmore, J. C. Brosheer, P. C. Gwinn, Ray Lawrence, and John W. Lefforge for analytical data presented in this paper.

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A NEW PLASTIC MATERIAL—AXF

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A new class of elastic plastic materials which are very resistant to the action of many solvents and chemical reagents may be prepared by reacting an ethylene dihalide in the presence of aluminum chloride with an aromatic hydrocarbon having the general formula $RC_6H_4R_1$. Certain of these products with a shearing plasticity at 65.5° C. of 40 to 80 (as measured by the Mooney shearing plastometer) have been designated "AXF." The properties of the plastic make it especially interesting as a compounding ingredient for use with natural or synthetic rubber.

The resistance to ozone cracking, the flexibility, and the breaking elongation of oil- and gasoline-resistant and semihard rubber stocks containing 15 to 20 parts of sulfur per 100 of rubber may be increased by the addition of AXF to the compound. A moderate amount of flexibility and stretch is possessed by hard rubber made from equal weights of rubber and AXF.

As a compounding material with DuPrene, AXF is superior to factice in several ways. AXF has an excellent plasticizing action both on DuPrene and on the ethylene polysulfide plastics known as Thiokol. With the latter, its inertness causes it to be preferred to rubber for use in this capacity.

RUBBER technologists are familiar with the increasing number of uses to which rubber has been put in recent years through modifications and adaptations effected by skilful compounding. At the same time, however, active research has been carried out, stimulated by the desire for new materials to meet still more exacting requirements—for example, greater resistance to oils and solvents and to oxidation. In general these investigations have taken one of two directions; they have been directed to a search for new synthetic rubber-like materials or to a study of new derivatives of rubber.

In both of these fields of research, achievements of outstanding importance have been disclosed. Whitby and Katz (*9*) reviewed and summarized the development work on synthetic rubber from its early beginnings. The announcement of poly-chloroprene or DuPrene by Carothers (*2*) and his associates was soon followed by recognition that this product is a synthetic rubber-like material with physical properties not only rivaling those of rubber but superior in many particulars in which rubber is most deficient. Various olefin-polysulfide reaction products have been described by Patrick (*6*) and, under the trade name of Thiokols, have been presented to the industry. Other synthetic products which have attracted the attention of rubber compounders include the glyptal resins (*10*), flexible phenol resinoids, and the recently announced Koroseal (*1*). A paper by Thies and Clifford (*8*) has summarized the reactions of the rubber hydrocarbon, apart from oxidation and vulcanization reactions.

Method of Preparation

A new class of elastic plastic materials, recently discovered (*7*), is prepared by reacting ethylene dihalide in the presence of aluminum chloride with an aromatic hydrocarbon having the general formula $RC_6H_4R_1$ where R and R_1 each represent hydrogen or a saturated aliphatic hydrocarbon radical containing more than one carbon atom. Aromatic hydrocarbons with only one carbon atom in the side-chain radical (as toluene or xylene) do not undergo this reaction to give plastic products. Suitable proportions of reactants include 1 mole of aromatic compound, 1 to 3 moles of ethylene dihalide, and up to 1 mole of aluminum chloride. By suitable control the reaction product can be varied from a very soft plastic with a shearing plasticity at 65.6° C. (150° F.) of 20 in the Mooney shearing plastometer (*5*) to a material having a shearing plasticity of more than 150. Products with milling, tubing, and calendering properties resembling those of rubber show a shearing plasticity in the range 40 to 80. This series of plastics has been given the designation AXF.

AXF does not react with sulfur, even after heating for an hour at 164° C. (327.2° F). This indicates the absence of aliphatic unsaturation. The structure of the products is unknown, but it seems probable that they comprise extensive chains and networks of benzene groups, each linked to at least two ethylene groups. Analysis for carbon and hydrogen shows 92.2 per cent carbon and 7.8 per cent hydrogen, and thus the empirical formula gives a 1:1 atomic ratio for carbon and hydrogen. Such a formula fits a polymer composed of $H_2C\cdot C_6H_4\cdot CH_2$ units or of $(H_2C)_2\cdot C_6H_2\cdot (CH_2)_2$ units as already suggested. *sym*-Diphenylethane has been isolated as a product from the earlier stages of the reaction.

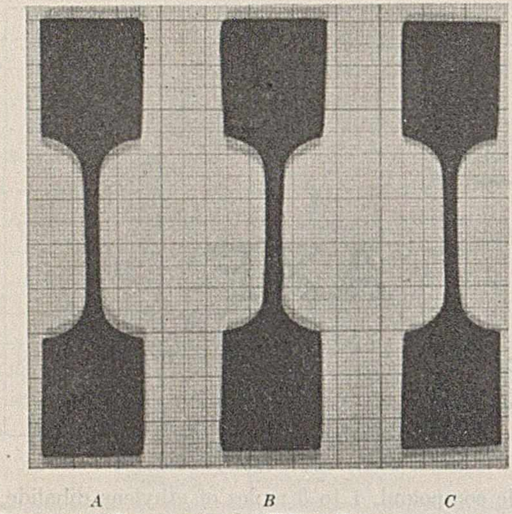

FIGURE 1. SWELLING OF AXF IN GASOLINE AND IN OIL

A. Not immersed.
B. Immersed in gasoline 5 days at room temperature.
C. Immersed in spindle oil 5 days at 70° C.

Physical Properties

The general physical properties of AXF plastic are outlined as follows:

Specific gravity	1.04
Ash, %	1.2
Color	Dark brown
Odor	Practically none
Hardening temp., ° C.	0
Tensile strength, kg./sq. cm. (lb./sq. in.)	Up to 32 (450)
Elongation, %	Up to 600
Action of acids and alkalies after immersion for 1 week at room temp.:	
Concd. HCl	No action
Concd. H_2SO_4	Swells and hardens slightly
50% H_2SO_4	No action
Concd. HNO_3	Attacked slowly
Glacial acetic acid	Swells moderately
50% NaOH	No action
NH_4OH (30% NH_3)	Surface bleached

AXF shows very low swelling in such solvents as ethyl alcohol, acetone, gasoline, kerosene, and light lubricating oils.

Figure 1 gives a comparison of a sample of AXF hydrocarbon with other AXF samples which have been immersed for 5 days in gasoline at room temperature or for 5 days in spindle oil at 70° C. There is some penetration of gasoline into the AXF as evidenced by the blister formation. The volume increase is 6.3 per cent for the sample immersed in gasoline and 3.4 per cent for the sample in oil.

On the basis of these properties, AXF has been investigated as a compounding material for use with rubber, DuPrene, or Thiokol. It will be shown that AXF may be combined with these plastics in proportions such as both to improve their processing characteristics and to give products with properties capable of withstanding more severe service conditions of certain types.

Processing Properties

Although AXF is generally used in connection with other plastics as an auxiliary compounding material, it may be of some interest to comment on its general processing properties. Grades of AXF having a Mooney shearing plasticity at 65.6° C. (150° F.) in the range 40 to 80 may be milled, calendered, and tubed in the same manner as well broken down rubber. Similar products of greater plasticity are more tacky and handle with greater difficulty.

Compounding Material with Rubber

In Figure 2 are shown comparative stress-strain curves for a pure gum type rubber compound with 3 parts of sulfur and for the same rubber compound with 40 parts of AXF added. The cures are for 5 minutes at 141° C. (286° F.). These curves show that the addition of this amount of AXF has but slight effect on tensile strength and ultimate elongation, and causes a small reduction in modulus. The compounding of rubber with large amounts of AXF does lower the tensile strength of the stock.

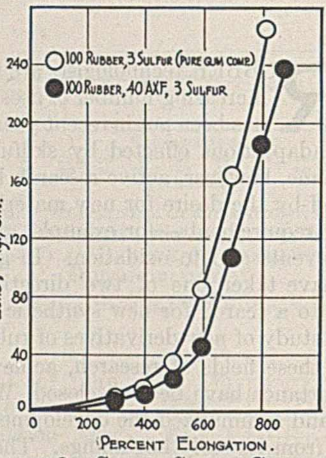

FIGURE 2. STRESS-STRAIN CURVES FOR PURE GUM RUBBER AND FOR AXF RUBBER

It is well known in the rubber industry that the compounding into a low-sulfur rubber stock of the various new oil-resistant synthetic rubbers has not been an effective means of developing an oil-resistant compounded rubber. AXF is accordingly not recommended as a compounding agent to promote oil resistance in a low-sulfur rubber compound. There are, however, interesting effects of AXF in low-sulfur rubber compounds. For example, a compound having rubber and AXF in the proportion 70:30 shows a reduction in rate of diffusion of air of more than 40 per cent as compared with the same compound without AXF.

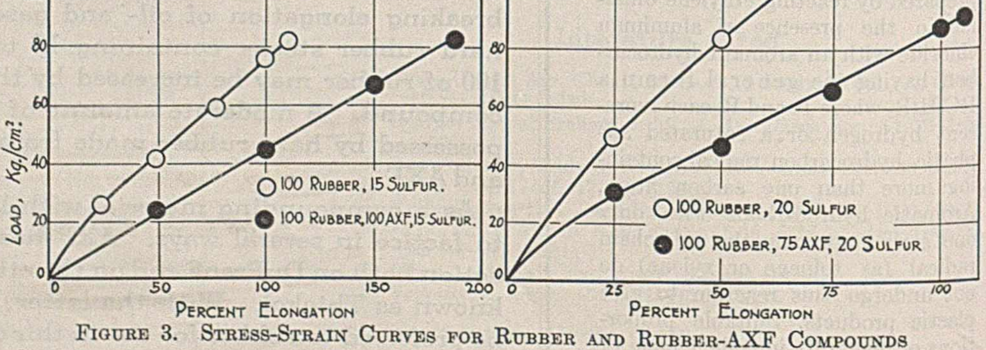

FIGURE 3. STRESS-STRAIN CURVES FOR RUBBER AND RUBBER-AXF COMPOUNDS

A more interesting application of AXF is in the development of flexible semi-hard rubber compounds of excellent oil resistance. Rubber compounds containing 15 to 20 parts of sulfur combined per 100 of rubber are known to have high resistance to swelling in gasoline or motor oils. However, such compounds have a sufficiently low breaking elongation so that they do not meet the requirements of flexibility for many types of service. Figure 3 shows comparative stress-strain curves of semi-hard rubber compounds with and without AXF. The higher breaking elongation of the AXF stocks is to be noted, particularly in the compound with 15 parts of sulfur per 100 parts of rubber.

Figure 4 shows a comparison of the effect of gasoline immersion for a period of 3 years of a semi-hard rubber AXF compound as compared with that for a heavily loaded rubber stock designed for service as an oil-resistant compound.

Table I gives the formula for a typical AXF-rubber compound of the type under discussion and indicates the percentage swelling of this compound in gasoline and in spindle oil.

TABLE I. EFFECT OF IMMERSING SEMI-HARD RUBBER-AXF COMPOUND IN SWELLING MEDIA FOR ONE WEEK

(Cured 75 minutes at 153° C.)

Rubber	100	Calcium oxide	10
AXF	75	Diphenyl guanidine	4
Zinc oxide	10	Sulfur	20
Carbon black	30	Antioxidant	2
Magnesium oxide	20		

Swelling Medium	Temp. of Test ° C.	Increase in Vol. %
Motor-grade gasoline	25	32.5
Light spindle oil	70	58.9

The oxygen aging characteristics of rubber compounds are not changed in any substantial degree by the presence of AXF in the compound. The use of a good rubber antioxidant, in the proportions ordinarily recommended in rubber compounding, affords adequate protection.

The ozone resistance of semi-hard rubber compounds such as described in Table I, with and without AXF, was compared. Very deep cracks formed in the rubber compound while practically none appeared in the AXF-rubber compound which received the same ozone exposure.

By compounding AXF in a hard-rubber stock in a 1:1 ratio with the rubber present, it is possible to combine moderate flexibility with the characteristic chemical inertness of hard rubber. A typical vulcanite compound is compared with a similar stock containing 100 parts of AXF (both cured 7 hours at 145° C.):

Compound:	OD	OF
Rubber	100	100
AXF	....	100
Zinc oxide	5	5
Magnesium oxide	5	5
Sulfur	45	45
Diphenyl guanidine	4	4
Tensile strength:		
Kg./sq. cm.	476.4	176.4
Lb./sq. in.	7060	2510
Elongation at break, %	5.5	15.0

Compounding Material with DuPrene

The investigation of the behavior of AXF as a compounding material with DuPrene has had the point of view of determining the possibility of improving the handling properties of the latter as well as of studying the effect upon the physical properties of the compounds. In connection with processing behavior, the milling, batch storing, calendering, and tubing properties were considered while the gasoline and oil resistance were examined carefully in connection with physical tests.

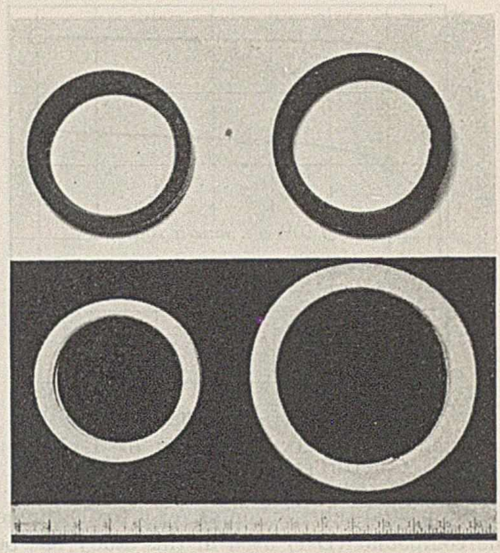

FIGURE 4. COMPARISON OF OIL-RESISTANT STOCKS

The black ring is semi-hard rubber which contains AXF; the white ring is a highly pigmented rubber compound. *Left,* rings as molded; *right,* after soaking in gasoline for 3 years.

Inasmuch as factice is recommended as a processing agent for improving the handling properties of DuPrene, a number of direct comparisons of AXF and factice have been made in various types of compounds.

Figure 5 shows a comparison of the change in plasticity during storage of a DuPrene-factice compound and a DuPrene-AXF compound. Although the shearing plasticities of the two compounds 24 hours after mixing were 69 and 62, respectively, the DuPrene-factice compound reached a plasticity of 105 in 14 days, whereas the AXF compound required 39 days to reach a plasticity of 109. Milling tests were made daily on a sample of each compound, and the final plasticity measurements were made on the date on which the compound had so set up that it was impracticable to mill it again. Both of the stocks are conventional compounds containing both zinc oxide and magnesium oxide within the range of amounts recommended for DuPrene stocks. The compounds differ only in the presence of factice or AXF.

The excellent plasticizing action which AXF shows in DuPrene stocks reduces the temperatures developed during milling, promotes smoothness of finish of calendered stocks, reduces calender shrinkage, and improves the tubing properties.

Figures 6 and 7 show the effects on gasoline and oil resistance of a typical DuPrene oil-resistant compound which may be

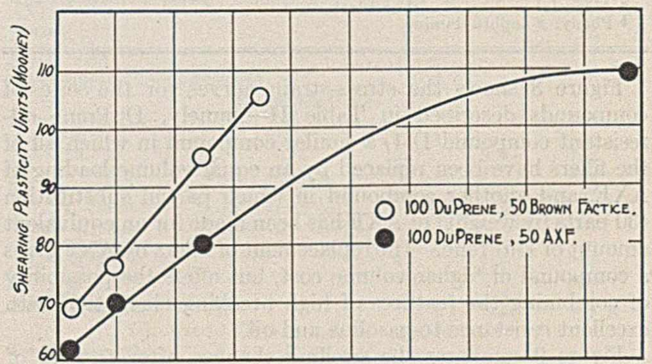

FIGURE 5. PLASTICITY CHANGES DURING STORAGE OF DUPRENE-AXF AND DUPRENE-FACTICE COMPOUNDS

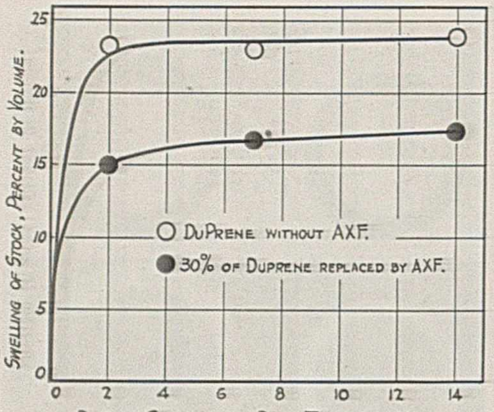

Figure 6. Gasoline Swelling of DuPrene and DuPrene-AXF Compound

obtained by partial substitution of AXF for DuPrene. The DuPrene compound (D-1) used in this study has been described by Hayden and Krismann (4). The 70 DuPrene–30 AXF compound shows approximately 30 per cent lower swelling in both gasoline and oil than does the DuPrene Compound D-1.

Table II gives the formulas and some physical properties of DuPrene compound D-1, a modified D-1 in which 30 per cent of the DuPrene was replaced by AXF, and another modification of D-1 in which all of the fillers were replaced by an equal volume of AXF.

Table II. Data on Oil-Resistant Compounds

[Cured 45 minutes at 141.7° C. (287° F.)]

	DuPrene D-1	Modified DuPrene D-1	
		Fillers replaced by AXF	70 DuPrene–30 AXF
Formulas			
DuPrene	100	100	70
AXF	...	52	30
Whiting	85	...	85
Gastex[a]	28.5	...	28.5
Glue	11.5	11.5	11.5
Zinc oxide	10	10	10
Light-calcined magnesia	10	10	10
Cottonseed oil	2	2	2
Wood Neozone rosin	5	5	5
Neozone D[b]	2	2	2
Sulfur	1.5	1.5	1.5
Properties Unaged			
Tensile strength:			
Kg./sq. cm.	91.4	98.1	72.9
Lb./sq. in.	1301	1395	1035
Max. elongation, %	410	740	250
Set, %	19	45	17
Properties after 5-Day Immersion in Spindle Oil at 70° C.			
Tensile strength:			
Kg./sq. cm.	74.5	53.4	50.4
Lb./sq. in.	1060	759	716
Max. elongation, %	370	750	210
Set, %	10	16	7
Swelling, % by vol.	45.4	49.6	33.7

[a] A special variety of carbon black.
[b] Phenyl-β-naphthylamine.

Figure 8 shows the stress-strain curves for the series of compounds described in Table II—namely, DuPrene oil-resistant compound D-1, a similar compound in which all of the fillers have been replaced by an equal volume loading of AXF, and another compound in which partial substitution (30 parts by weight) of AXF has been made for an equivalent amount of DuPrene. The replacement of fillers by AXF gives a compound of higher volume cost, but offers the possibility of combining the features of high breaking elongation with excellent resistance to gasoline and oil.

Figure 9 compares the swelling changes after 5 days of immersion in spindle oil at 70° C. of a DuPrene-AXF and a DuPrene-factice compound. The dimensions of the test sample before immersion are also shown for comparison. The DuPrene-factice compound is based on compound 236[1] described in the DuPrene Manual (3). The formulas are as follows:

	DuPrene-Factice	DuPrene-AXF
DuPrene	100	100
Soft brown factice (hardness 10)	150	...
AXF	...	150
Thermax[a]	370	370
Zinc oxide	10	10
Light-calcined magnesia	10	10
Rosin	1	1
Soft cumar[b]	10	10
Cottonseed oil	5	5
Neozone D	2	2

[a] A special variety of carbon black.
[b] p-Coumarone resin.

The use of AXF in DuPrene is not recommended where the highest tensile strength and abrasion resistance are required. Tests have shown no evidence that either the oxygen or heat-aging of DuPrene compounds is impaired by the presence of

Table III. Physical Tests of AXF in DuPrene Compounds

Formula of Compound BP

DuPrene	60	Sulfur	0.5
AXF	40	Cottonseed oil	2
Light-calcined magnesia	5	Neozone D	2
Zinc oxide	5	Carbon black	42.8
		Wood rosin	5

Tensile Strength

Cure at 141.7° C.	Unaged		96 Hr. in Oxygen at 70° C.		1 Week in Gasoline at Room Temp.		1 Week in Spindle Oil at 70° C.	
Min.	*Kg./sq. cm.*	*Lb./sq. in.*	*Kg./sq. cm.*	*Lb./sq. in.*	*Kg./sq. cm.*	*Lb./sq. in.*	*Kg./sq. cm.*	*Lb./sq. in.*
15	112.1	1595	106.9	1520	108.3	1540	78.8	1120
30	115.8	1645	109.7	1560	111.8	1590	79.5	1130
45	116.8	1660	110.4	1570	111.1	1580	80.2	1140
60	119.5	1700	109.7	1560	113.9	1620	80.9	1150
75	116.8	1660	112.5	1600	106.2	1510	80.9	1150
90	117.4	1670	102.0	1450	108.3	1540	85.2	1210

Maximum Elongation, Per Cent

15	330	250	310	310
30	330	240	300	300
45	320	230	290	290
60	320	230	300	290
75	290	240	270	280
90	310	220	280	280

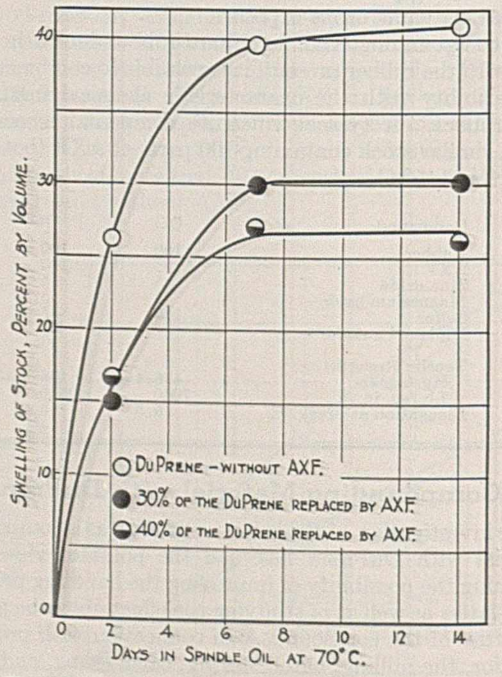

Figure 7. Oil Swelling of DuPrene and DuPrene-AXF Compound

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[1] This particular compound modification was suggested by a member of the development staff of the Rubber Chemicals Division of E. I. du Pont de Nemours & Company, Inc.

AXF. There is evidence that the high ozone resistance of DuPrene is enhanced when AXF is added to a DuPrene compound.

DuPrene-AXF compounds show higher tensile strengths as the carbon black loading is increased. In a 60 DuPrene–40 AXF stock, as the volume loading of carbon black is increased from 20 to 40 volumes on 100 volumes of DuPrene-AXF plastic, the tensile rises from approximately 100 to 150 kg. per square cm.

Table III shows several physical properties over a range of cures of a typical DuPrene-AXF compound loaded with carbon black.

AXF has also been found very resistant to the action of lithographic varnishes. The swelling of AXF in a commercial lithographic varnish after 5 days' immersion amounted to only 1.5 per cent. This feature has been used to advantage in compounding with DuPrene to prepare products which are particularly adapted to use in printers' blankets and inking rollers for some types of work.

Compounding Material with Thiokol

Some studies on the effect of compounding AXF with the several commercial olefin polysulfide plastics have been made. With certain types of these plastics, it has been recommended that small percentages of rubber be added to assist in processing operations.

It has been found that amounts of AXF as high as 20 per cent by weight may be compounded into these plastics to give products more readily processed, with somewhat higher breaking elongation and the same high resistance to gasoline and oils characteristic of the olefin polysulfide plastics when processed alone. Table IV shows the physical properties of several Thiokol compounds with rubber and with AXF.

A new type of olefin polysulfide plastic recently introduced (Thiokol D) is highly resistant to mill breakdown. It has been found that the introduction of approximately 20 parts by weight of AXF to 100 parts of Thiokol plastic effects a reduction in milling time of a standard Thiokol D compound from 40 to 15 minutes for a 500-gram mix on a laboratory mill.

AXF reduces the shearing plasticity of Thiokol, as shown by the following data:

	Milling Time, Minutes	Mooney Plasticity Units at 100° C. (212° F.)
Standard Thiokol D	40[a]	172
Thiokol D + 10 AXF	15	126
Thiokol D + 20 AXF	15	81

[a] The longer milling time with the standard Thiokol D compound was necessary to get the mix into sheet form.

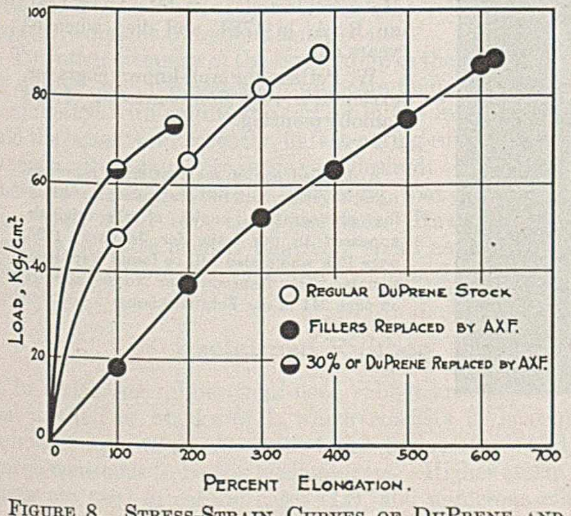

Figure 8. Stress-Strain Curves of DuPrene and DuPrene-AXF Compounds

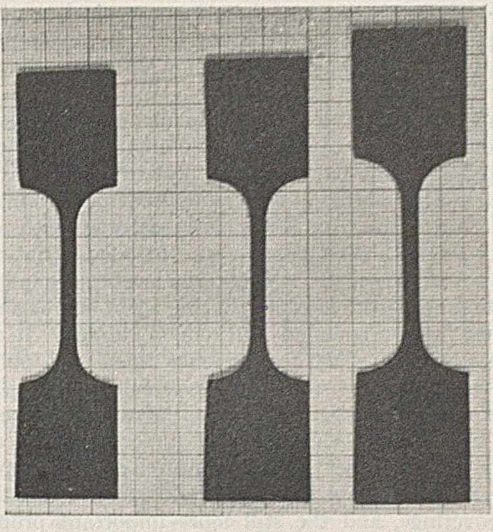

Figure 9. Swelling Resistance of DuPrene-Factice and DuPrene-AXF Compounds

A. Test sample, not immersed.
B. DuPrene-AXF, immersed in spindle oil 5 days at 70° C.
C. DuPrene-factice, immersed in spindle oil 5 days at 70° C

Table IV. AXF vs. Rubber in Thiokol A Compounds

(Cured 60 minutes at 141° C.)

Formula	BQ	BR	CY
Olefin polysulfide plastic, Thiokol A	100	100	100
Rubber	5	20	....
AXF	....	....	20
Diphenyl guanidine	0.25	0.25	0.25
Tetramethylthiuram disulfide	0.10	0.10	0.10
Zinc oxide	10	10	10
Stearic acid	0.5	0.5	0.5
Properties Unaged			
Tensile strength:			
Kg./sq. cm.	53.7	60.6	49.0
Lb./sq. in.	764	862	697
Max. elongation, %	220	350	290
Set, %	20	52	43
Immersed 7 Days in Gasoline at Room Temperature			
Tensile strength:			
Kg./sq. cm.	50.5	48.8	46.2
Lb./sq. in.	718	694	657
Max. elongation, %	220	290	270
Set, %	22	26	35
Vol. increase, %	0.0	25.8	0.0
Immersed 7 Days in Spindle Oil at 70° C.			
Tensile strength:			
Kg./sq. cm.	47.7	43.8	42.8
Lb./sq. in.	678	623	608
Max. elongation, %	200	240	230
Set, %	20	22	24
Vol. increase, %	1.2	29.5	0.0

Table V. Effect of AXF in Thiokol D Compounds

(Cured 30 minutes at 141° C.)

Formula	OH	NZ	OA
Olefin polysulfide plastic, Thiokol D	100	100	100
AXF	...	10	20
Gastex	55	55	55
Zinc oxide	10	10	10
Stearic acid	0.5	0.5	0.5
Altax dibenzothiazyl disulfide	0.3	0.3	0.3
Properties Unaged			
Tensile strength:			
Kg./sq. cm.	72.3	60.7	52.2
Lb./sq. in.	1027	864	742
Max. elongation, %	450	470	480
Set, %	17	18	19
Immersed 7 Days in Gasoline at Room Temperature			
Tensile strength:			
Kg./sq. cm.	46.5	54.0	40.6
Lb./sq. in.	660	768	577
Max. elongation, %	460	510	520
Set, %	20	25	34
Vol. increase, %	2.1	2.2	2.8
Immersed 7 Days in Spindle Oil at 70° C.			
Tensile strength:			
Kg./sq. cm.	32.7	45.4	33.0
Lb./sq. in.	464	646	469
Max. elongation, %	420	520	530
Set, %	21	23	31
Vol. increase, %	1.4	2.8	2.8

Table V shows the test data for a typical compounded olefin polysulfide plastic (Thiokol D) and for similar compounds to which 10 and 20 parts of AXF, respectively, were added.

No attempt has been made in this paper to discuss all the possible applications of AXF as a compounding material. It is desired to point out that the process for preparing the material has been brought under such control as to make possible the preparation of a type of material with uniform physical properties but capable of controlled variation as to hardness and viscosity. The material has been found to have interesting properties as a plasticizing agent and as a stabilizing agent for compounded DuPrene in storage. It also has distinct possibilities as a processing agent for polysulfide plastics and enhances some of their useful properties.

More recent investigations which have not yet been concluded suggest that AXF may find important application in the wire insulation field. These features of AXF application include improvements in the oil and solvent resistance of cable coverings, and the still more important property of high resistance to electrical breakdown. Details of these developments will be reserved until such time as a more complete quantitative study has been made.

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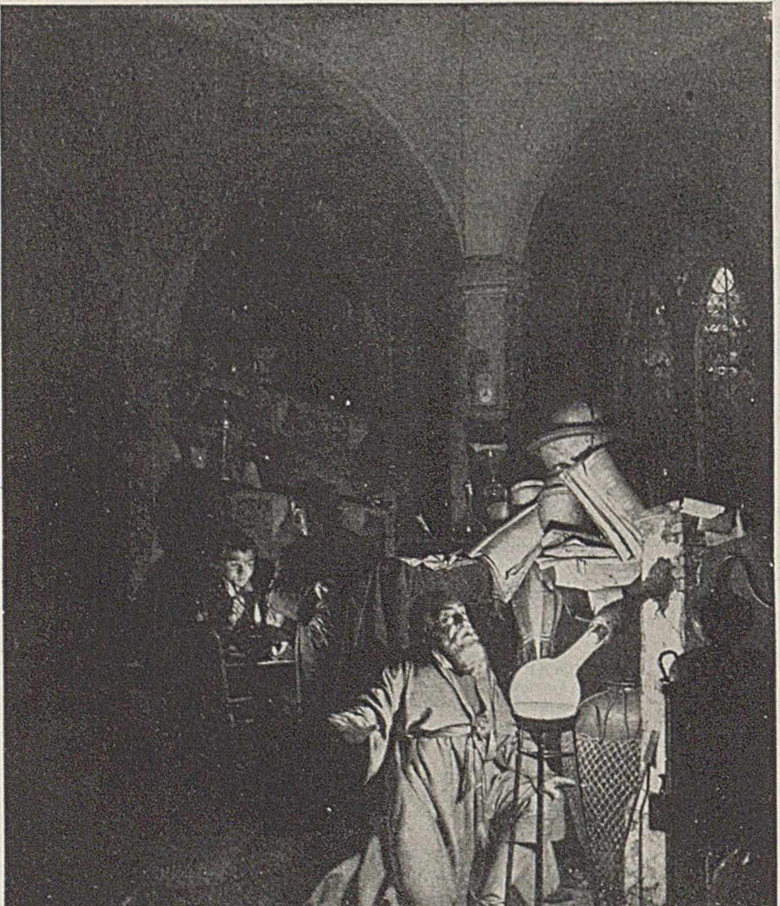

The Alchymist—

By Joseph Wright

The original of this, No. 63 in the Berolzheimer series of Alchemical and Historical Reproductions, is in the Museum and Art Gallery of Derby, England, the native city of the artist. It was painted about 1771, having been shown in the Exhibition of the Society of Artists of Great Britain of that year.

According to the artist, this painting represents "The Alchymist, in search of the Philosopher's Stone, discovers Phosphorus, and prays for the successful conclusion of his operation, as was the custom of the Ancient Chymical Astrologers."

Joseph Wright, commonly known as "Wright of Derby," was born in 1734. His work was largely portraiture and landscape. He studied in London under Thomas Hudson, the teacher of Reynolds, and achieved his best results in the portrayal of artificial light. He was elected an A. R. A. in 1781, an R. A. in 1784, and died when 63 years old.

W. Pether, the well-known engraver, executed a very fine engraving of this famous painting.

A detailed list of the first sixty reproductions, together with full particulars for obtaining photographic copies of the originals, appeared in our issue for January, 1936, page 129, where also will be found Reproduction No. 61. Reproduction No. 62 appears on page 241 of our February issue.

ONWARD MARCH OF RUBBER

The latest advances in the field of rubber compounding are reviewed and discussed briefly, with special emphasis on vulcanizing agents, acidic compounding ingredients, softeners, organic accelerators, antioxidants, and reinforcing powders. Progress in the use of rubber as a raw material for the manufacture of synthetic products is described. New rubber-like materials recently developed as substitutes for, or adjuncts to natural rubber, receive attention, as does reclaimed rubber. Some of the newer applications of latex are illustrated, as well as some of the more important new uses of rubber and new designs for rubber products.

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IN A previous paper (*33*), delivered in the fall preceding "A Century of Progress," the writer reviewed the outstanding advances in the rubber industry during the previous century. Cited as the most important discoveries since that of vulcanization in 1839 were the method of reclaiming vulcanized rubber scrap (1899), the value of acidic materials in compounding (1904), organic accelerators (1906), reinforcing pigments (1912–1915), and antioxidants (1918–1923). It will be the purpose of this paper to cover briefly the present status in these fields, and to point out some of the more recent advances in other fields related to rubber.

Vulcanizing Agents

Sulfur continues to be the chief vulcanizing agent; very few commercial rubber products are compounded without it. There are some exceptions—for example, certain virgin crepe soles, which are used in the unvulcanized state, and thin articles vulcanized with sulfur chloride.

The thiuram disulfide accelerators effect vulcanization without the addition of any free sulfur. Various investigators have assumed, probably correctly, that these catalysts of vulcanization split off sulfur during the cure, thus supplying the necessary vulcanizing agent. For reasons of economy these thiuram disulfides are ordinarily used in conjunction with some free sulfur; otherwise a high concentration of the expensive organic compound must be used.

Two other elements of the same group in the periodic system as sulfur—selenium and tellurium—are finding application in conjunction with sulfur, the former in the insulation of wire and the latter, very recently, in fast-curing rubber compounds where unusual aging properties are desired. The use of both these elements appears to be increasing, that of tellurium at a somewhat faster rate than selenium. However, the total tonnage of these used is relatively small as compared with the enormous volume of sulfur consumed by the rubber industry.

Reclaimed Rubber

In reclaiming rubber from used rubber articles, the original method of Marks (*21*), which consists in heating the rubber scrap with caustic soda at high temperatures and pressures, continues to be the basic process. Higher steam pressures are used in certain cases (*14*), and numerous oils and softeners have been introduced, but basically the process is unchanged. The oils soften and swell the rubber; the caustic disintegrates the fabric. It was formerly thought that the caustic also removed what free sulfur remained in the scrap, but it is now known (*34*) that the high temperatures used in reclaiming rubber combined the free sulfur with the rubber before the caustic penetrates sufficiently to dissolve any appreciable amount of it.

Recent advances in this field consist largely in processing to obtain smoother products of greater uniformity that will disperse more readily in the new rubber to which they are added when fabricated into new rubber articles.

Acidic Compounding Ingredients

There has been much activity in the past few years in the search for cheaper acidic compounding materials, which are required for bringing out the highest activity of certain organic accelerators and enhancing the quality of the product, for softening the rubber to the point necessary for satisfactory dispersion of the reinforcing powders, and for imparting the desired workability, molding, and tubing properties to the unvulcanized batch.[1] Stearic acid from animal fats has been almost universally used and still remains the most important material for this purpose, but large quantities are now obtained from sources other than animal fats, and other fatty acids of the same homologous series are finding application. Examples are lauric acid from coconut oil, the acids obtained from hydrogenated fish oils, the mixed acids from cottonseed foots, and also press-cake acids—that is, solid acids obtained by chilling the mixed acids from various plant fats and oils. Mixed acids obtained from petroleum by

[1] In this connection, the paper by I. Williams and C. C. Smith, "Hydrazines as Rubber Softeners" [IND. ENG. CHEM., **27**, 1317–21 (1935); U. S. Pat. 2,018,643 (Oct. 22, 1935)], should be mentioned. Methods of reducing the amount of mechanical working that must be done in processing rubber are of vital interest to the rubber chemist. However, the use of a hydrazine in rubber compounding is not new [R. B. Naylor, U. S. Patent 1,418,825 (1922); S. M. Cadwell, *Ibid.*, 1,556,415 (1925)]. The toxicity of this class of compounds (Beilstein, Handbuch der organischen Chemie, 4th ed., Vol. XV, p. 106, Berlin, J. Springer, 1932) and their cost have, up to the present time, limited their practical application.

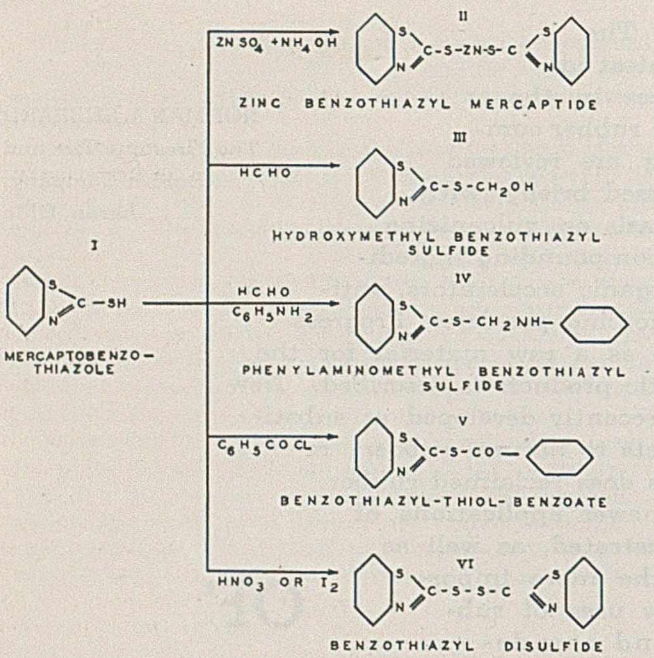


Figure 1. Mercaptobenzothiazole and Related Compounds Used as Organic Accelerators of the Vulcanization of Rubber

oxidation are also now available to the rubber compounder. Many of these products can replace animal stearic acid in certain rubber batches with entirely satisfactory results and considerable lowering of costs.

Organic Accelerators

In the past few years no new class of organic accelerators has been discovered; or, if any has been, the discovery has not been made public nor has the product been made available to the industry. Mercaptobenzothiazole or its derivatives, together with the substituted aryl guanidines and the aldehyde amines, still constitute the main classes of accelerators of moderate speed; and the dithiocarbamates and thiuram mono- and disulfides are still the chief ultra-accelerators. The very recent additions to the commercial accelerators (Figure 1) have been chiefly derived from mercaptobenzothiazole, I—for example, the zinc salt, II; formaldehyde derivative (*20*, *41*), III; the reaction product with formaldehyde and aniline (*9*), IV; the benzoyl compound (*15*), V; and the oxidation product (*29*), VI.

Much progress has been made in the use of organic accelerators. Where formerly one organic chemical was ordinarily used to accelerate a rubber batch, now two materials are often employed, obtaining the joint effects of the two accelerators not only as regards acceleration itself, but as regards cured properties, for different accelerators have specific effects on certain physical properties of the vulcanized product.

In some cases one accelerator activates another; that is, the result is not purely additive. Such combinations may lower acceleration costs and produce peculiarly valuable properties.

Reinforcing Powders

The search for new and better reinforcing agents occupies much of the time and thought of the rubber chemist. Carbon black still holds first position among reinforcing powders, and much effort is being expended in learning how to use more effectively its enormous surface activity in order to improve the wear resistance of tire treads. Keeping pace with the rapidly increasing demands of the automotive engineer requires continuous intense activity on the part of the research and development staffs of the rubber industry.

The producers of rubber blacks, under pressure from the consumers of their products, are making blacks far superior to those produced in the twenties. New standards of uniformity and freedom from grit have resulted. They have also materially assisted the rubber factories in improving the appearance of their mill rooms by largely removing the dust nuisance during the incorporation of the black in the rubber. The past few years have seen the introduction and adoption of the so-called dustless blacks (*2*, *39*). One of these is a form of black densified by a violent mechanical action which frees it from a considerable portion of its air and rolls it into small spherical pellets sufficiently compact to be relatively dustless (Figure 2).

Perhaps the most interesting of the newer reinforcing agents are the new whitings (*7*, *26*). Calcium carbonate is precipitated in the presence of a protective colloid, under such carefully controlled conditions of concentration and temperature that it comes down in a very fine state of subdivision and the particles do not tend to grow. One of them is so fine that almost all of it is 0.5 μ or less in particle size (Figure 3), while ordinary whiting runs from 2.0 to 4.0 μ, with agglomerates as large as 20 μ (Figure 4). They promise to find a very definite place in the economy of the rubber compounder.

Mention should also be made of certain zincated barium sulfates which have recently been offered.

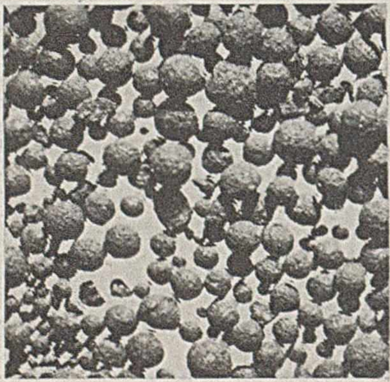


Figure 2. Rubber Channel Black, Pelleted to Render It Relatively Dustless

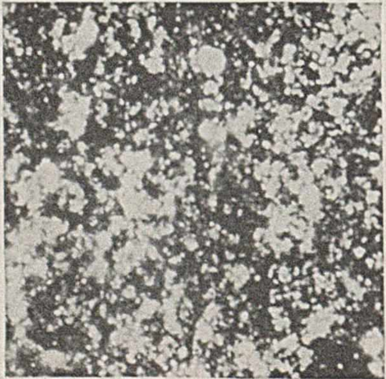


Figure 3. Special Whiting Precipitated in the Presence of a Protective Colloid

Figure 4. Ordinary Precipitated Whiting

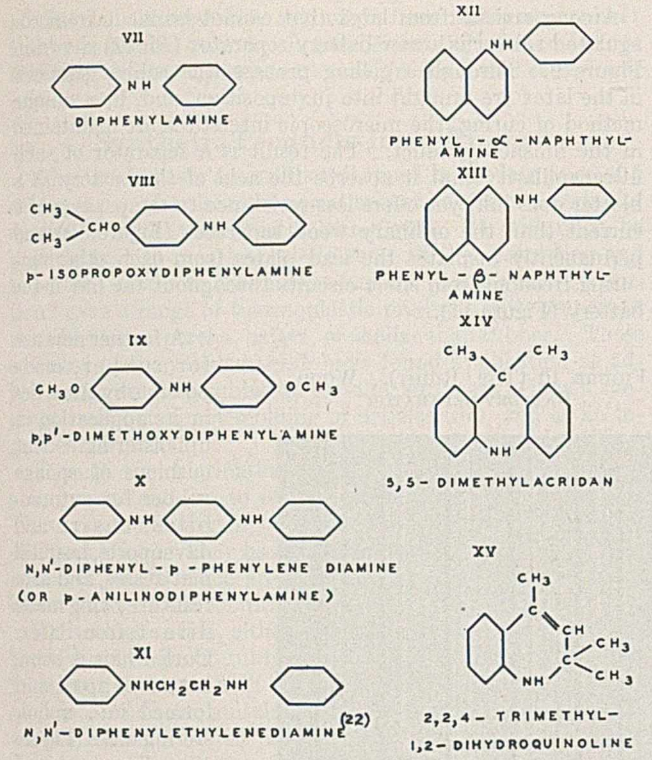


FIGURE 5. SECONDARY AROMATIC AMINES USED AS ANTIOXIDANTS FOR VULCANIZED RUBBER

Antioxidants

Practically all of the chemical compounds (Figure 5) used commercially as oxygen inhibitors or antioxidants for vulcanized rubber are secondary aromatic amines, many of them closely related to diphenylamine, VII. Among the most recent ones are *p*-isopropoxy diphenylamine (*32*), VIII; the corresponding *P,P'*-dimethoxy compound, IX; and *N,N'*-diphenyl-*p*-phenylene diamine (*8*, *10*, *31*), X. Both the alpha- and beta-phenylnaphthylamines, XII and XIII) continue to be used in large quantities, as does also a mixture of diphenylamine with 5,5-dimethylacridan (*17*, *30*), XIV, and other substances. This acridan and the dihydroquinoline (*28*), XV, are acetone condensation products of diphenylamine and aniline, respectively. All of these compounds not only preserve the tensile strength and elasticity of rubber, but also definitely reduce the tendency for highly compounded stocks, such as tire tread stocks, to crack when subjected to repeated and severe flexing. Especially interesting from this latter standpoint is the *N,N'*-diphenyl-*p*-phenylene diamine. The beneficial influence of this material is illustrated in Figure 6, which shows strips of tread stocks after severe flexing.

A very recent contribution to our knowledge of antioxidants (*36*) concerns mixtures of secondary amines with hydroquinone or pyrogallol. Using triethanolamine with this combination gave enhanced resistance to flex cracking.

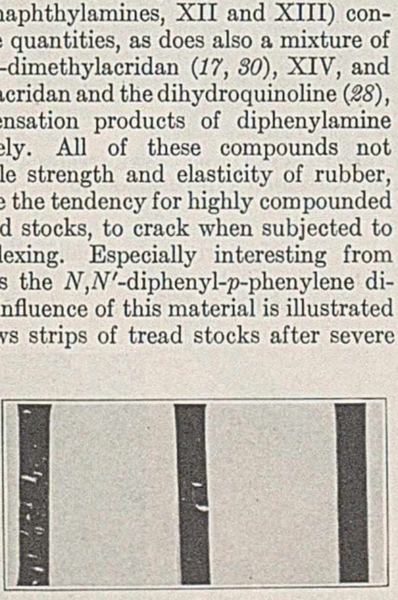


FIGURE 6. TIRE TREAD STOCKS

A. No antioxidant.
B. 1 part of a standard antioxidant to 100 parts of rubber
C. 0.7 part of the same antioxidant with 0.3 part *N,N'*-diphenyl-*p*-phenylene diamine to 100 parts of rubber.

New Rubber Substitutes or So-Called Synthetic Rubbers

Space will permit no more than brief reference to these products, however interesting and remarkable they may be. Nor is it necessary to give more than passing mention to DuPrene in order to recall the remarkable chemical engineering feat that this product represents. Based on the purely scientific work of Nieuwland (*23*), a product (*5*, *6*) has been developed so closely resembling rubber in its physical characteristics that it is easily the most outstanding recent scientific development in the field of rubber. It is a misnomer to call it "synthetic rubber," since it is not a hydrocarbon and differs considerably from rubber in behavior. In spite of its present high price, it is filling a real need in the rubber industry owing to its remarkably low absorption of petroleum products in the entire range from gasoline to lubricating oils, and is now going into oil-resistant gaskets, gasoline hose, and similar articles.

Another product, also highly oil-resistant, is that produced by the action of polysulfides on ethylene dichloride, and known as Thiokol (*24*). Recently, modifications have been made that are, to a considerable extent, freed from the highly obnoxious odor of the original product, and the commercial possibilities are thereby much extended.

Other synthetic products are bidding for notice in this field—for example, a product made from benzene and ethylene dichloride in the presence of aluminum chloride (*35*).

Latex

The current literature, both journal and patent, is redundant with reference to the direct use of rubber latex. Each year sees new uses and applications of rubber in this form in which it comes from the rubber tree. Preserved with ammonia and shipped either in its original concentration (approximately 38 per cent rubber content) or concentrated either by centrifuging, creaming, or evaporating to approximately 60–70 per cent dry rubber content, this colloidal suspension offers seemingly unlimited possibilities in making unique and quality rubber products. In many cases—for example, in the manufacture of tire inner tubes—it has failed to compete with ordinary plantation rubber (acid-coagulated), owing to its higher price in this form, but only for this reason and the higher manufacturing costs, for ex-

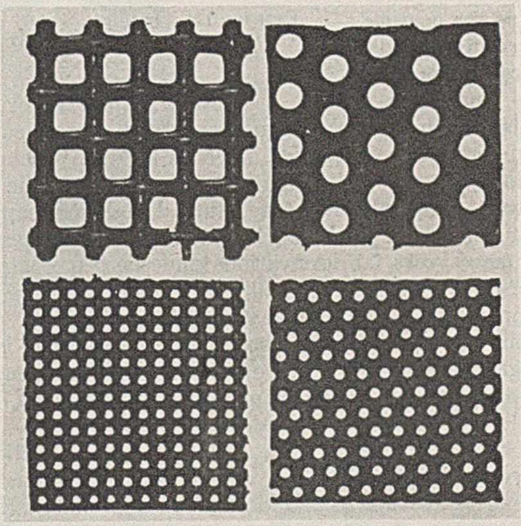

Courtesy, American Anode, Inc.

FIGURE 7. METAL SCREENS AND GRIDS COATED WITH RUBBER BY ELECTRODEPOSITION FROM LATEX

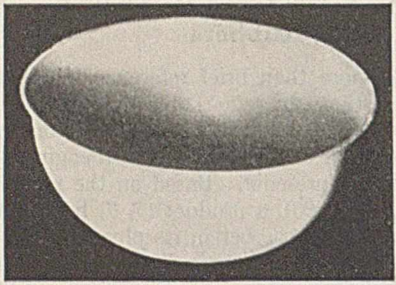


Figure 8. Rubber Article Made by Dipping a Heated Form in Heat-Sensitized Latex

cellent inner tubes can be made from latex, either by electrodeposition, heat coagulation on forms, or filtration.

In many cases, however, this price situation does not retard the use of latex—as for example, where expensive solvents are eliminated in the manufacture of dipped goods; also many products can be made from latex which are sufficiently higher in quality to warrant the extra cost, or which cannot be made at all direct from crude rubber. Such goods as surgeons' and linemen's gloves, and numerous other dipped goods are in regular production from latex. Electrodeposition (*1*) makes possible the coating of screens, grids (Figure 7), propeller blades, and other articles of unusual shape. Latex, heat-sensitized with certain inorganic salts, will give deposits on heated forms or molds of as much as 0.1 inch thickness in one dip of a few seconds (Figure 8). According to the patent literature (*25*), rubber tubing, thread, bathing caps, and similar thin rubber goods may be made by such a process.

Figure 9 (Top, Left). Rubber Battery Separator from Latex

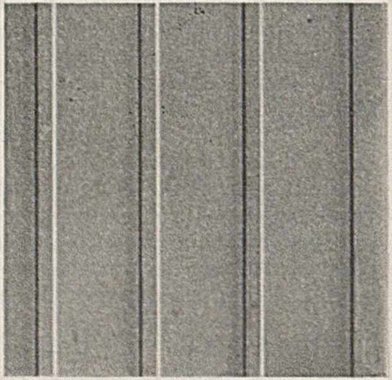
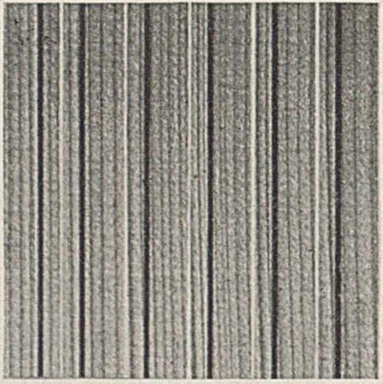
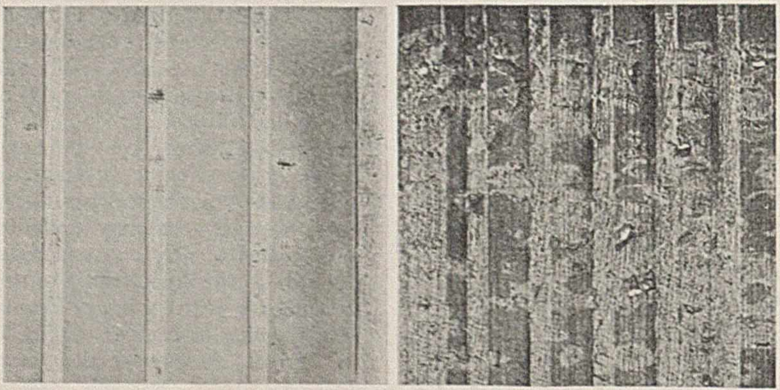


Figure 10 (Top, Right). Wood Battery Separator





Courtesy, Firestone Tire & Rubber Company

Figure 11. Rubber (*Left*) and Wood (*Right*) Separators Taken from a Battery That Had Been Repeatedly Charged and Discharged

For many years, fabric of various kinds has been coated with rubber by dipping in latex, and, if the modern wetting agents are employed, definite impregnation may be obtained.

In the same category may be mentioned the use of latex in impregnating various fibrous products, such as cotton, wood pulp, and asbestos in the manufacture of shoe soles, paper, brake lining, abrasive and polishing wheels, etc.

Rubber thread, of minute and round cross section (as opposed to the coarser square thread made by cutting calendered sheet), is now a standard rubber product. This is made by extruding properly compounded latex through tiny orifices into acetic acid, in much the same way as rayon is made by forcing cellulose solutions through spinnerets into coagulating media.

Among articles from latex that cannot be made from coagulated rubber is a new battery separator (*13, 27*) shown in Figure 9. Through a gelling process, the rubber particles in the latex are brought into juxtaposition, and, by a unique method of curing, the microscopic interstices are maintained in the finished product. The result is a separator of such ultracapillarity that it absorbs the acid of the battery as a blotter does ink, yet offers less resistance to the passage of a current than the ordinary wood separator (Figure 10) and permanently insulates the lead plates from each other, insuring freedom from short circuits throughout the life of the battery (Figure 11).

A further new use for rubber, made possible by latex, lies in its application in upholstering. Seat cushions of sponge rubber for automobiles, chairs and davenports, hospital mattresses, and arm rests are being made direct from latex. Curled hair is being latex-dipped and formed into upholstering units (Figure 12). The backs of rugs and carpets are being treated with latex to rubber-set the pile, make every cut edge substantially a selvage edge in behavior, and allow the insertion of designs so popular in modernistic interior decorating.

The replacement of rubber cements containing gasoline or other solvents by latex cements is rapidly materializing, as witnessed by the use of latex cements in leather as well as rubber shoe manufacturing, can sealing, and for various adhesive purposes. Such cements have the advantage of high rubber content with low viscosity. In this connection, the use

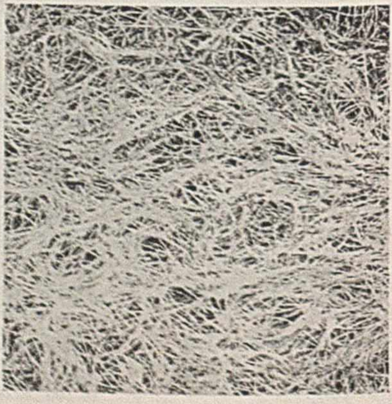


Figure 12. Section of a Seat Cushion Made from Latex-Dipped Curled Hair

Courtesy, Armour and Company

of artificial "latices" (*19*, *38*), made from masticated rubber and/or reclaimed rubber, should be mentioned as means of obtaining greater adhesiveness and, in the latter case, lower costs as well.

Synthetic Products from Rubber

When a few years ago rubber dropped to the low price of 5 cents per pound or less, the use of rubber as a raw material for synthetic work was greatly stimulated. It will only be possible here to mention briefly some of the interesting and important products that have resulted. Catalytic "cyclization" gave a range of thermoplastic products with properties more like gutta-percha, balata, or shellac than rubber. These so-called "polycyclo-rubbers" have found application as adhesives for sticking rubber to metallic surfaces (*11*), as a synthetic resin for direct molding of articles (*37*), and as an ingredient for paints.

Through the chlorination of rubber, products of very high chlorine content (up to 68 per cent) (*18*, *40*) are obtained. These products vary in properties, depending on the degree of chlorination. They have found application for use in noncorrosive paints which are highly resistant to acids, alkalies, and severe weather conditions.

Hydrochlorination, either by passing hydrochloric acid gas through solutions of rubber in solvents (*3*, *4*), or by direct treatment of rubber with liquid hydrochloric acid (*12*), yields addition products containing up to approximately 34 per cent of chlorine. Such products are being exploited for use in transparent papers. The films formed are highly impervious to water and promise to find application for wrapping all kinds of merchandise—for example, food products, where either retention of moisture content (baked goods) or exclusion of moisture (candies) is highly desirable.

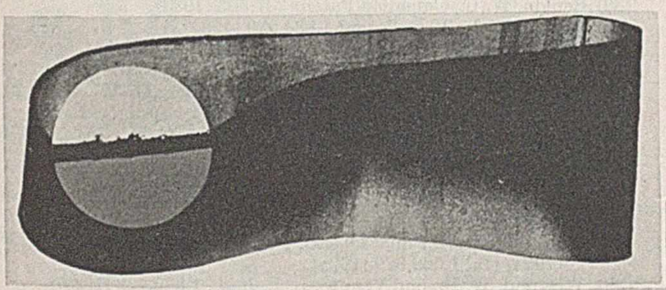


Figure 14 (Above). Cross Section of Inner Tube with Impervious Ply to Reduce Air Loss
Courtesy, Firestone Tire & Rubber Company

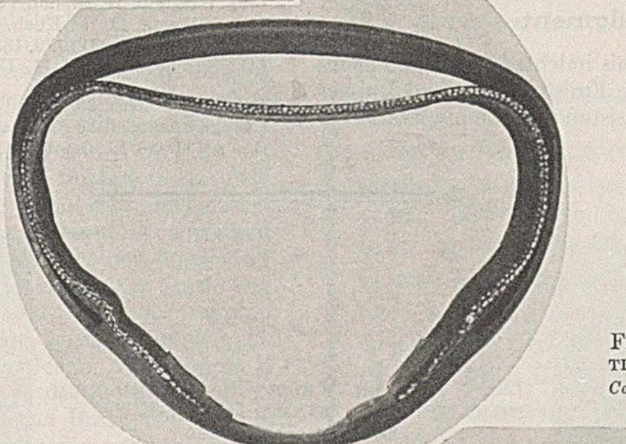


Figure 15 (Center). Cross Section of Tube Which Reduces the Rate of Escape of Air in Case of Puncture
Courtesy, Goodyear Tire & Rubber Company

New Product Developments

New applications of rubber are by no means confined to products made from latex. Each year sees more and more use of rubber in damping vibration and eliminating noise. The use of rubber in the automobile for motor mountings, spring shackles, etc., is so well known as hardly to require mention, but the use of rubber in mounting stationary machinery, both heavy and light, is perhaps less known (Figure 13). The world is rapidly becoming vibration and noise conscious, and rubber is playing and will continue to play a major part in combating these enemies of health and efficiency.

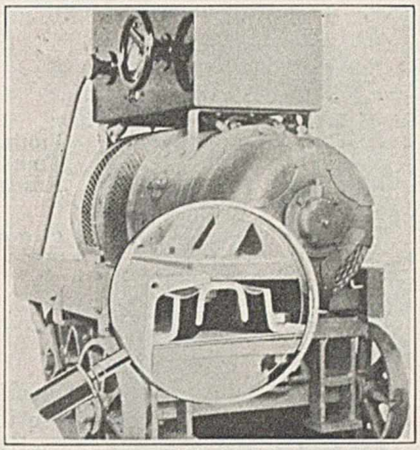


Figure 13. Motor Generator Set Mounted on Truck with Vibration Dampener to Eliminate Noise and Vibration, and to Cushion Equipment against Jolts and Jars
Courtesy, Firestone Tire & Rubber Company

Much might be said about improvements in tire design to increase both safety and utility. From the latter standpoint a recent innovation in tread design (*16*), eliminating the necessity of chains even under what were heretofore almost "unnavigable" road conditions, is illustrated in Figure 17.

Finally, new developments in tube stocks and tube design should be mentioned—tubes with markedly reduced air loss giving smoother and slower tire tread wear (Figure 14), tubes which reduce the rate of escape of air in case of puncture (Figure 15), and puncture-proof tubes (Figure 16). These are important contributions of the rubber industry for the protection of the motorist, and, with the casualty records, can it be questioned that he needs such protection?

After this brief review, we cannot doubt that rubber is marching onward and will continue to march onward to meet the ever increasing demands of civilization. Has rubber reached its peak of usefulness? The writer feels he can, with all assurance, answer "No." However re-

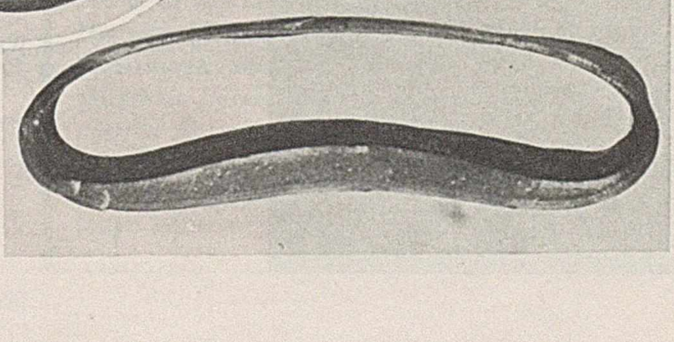


Figure 16 (Below). Cross Section of a Puncture-Proof Tube
Courtesy, Firestone Tire & Rubber Company

Figure 17. New Rugged Tire Tread Design with Remarkable Traction Quality

Courtesy, Firestone Tire & Rubber Company

markable the strides made in the past, the progress will continue, both through empirical and scientific investigation. Cut-and-try methods will not bring the results that they have in the past, but they will bring results, and the more fundamental scientific investigations, which are now in progress in the efficient, well-manned research laboratories and development departments of the larger rubber companies, as well as of those industries producing chemicals and materials for the rubber industry, will bring to light new facts and fundamental principles that may even revolutionize the industry. The present investigations on the use of rayon, in place of cotton, to produce a tire which will withstand still better the punishment received in high-speed, high-temperature service, are indicative of what revolutionary moves are in the offing. It is possible even now to make a pneumatic tire without using a pound of cotton or rubber, the body of the tire being made of rayon from wood pulp and the rubber being replaced by DuPrene from coal, limestone, and common salt. Practical? No, not yet! But who can say that the obstacles of cost and manufacturing difficulties will not be overcome?

Acknowledgment

The writer wishes to express his indebtedness to the members of the research staff of The Firestone Tire and Rubber Company for their invaluable assistance in the preparation of this paper.

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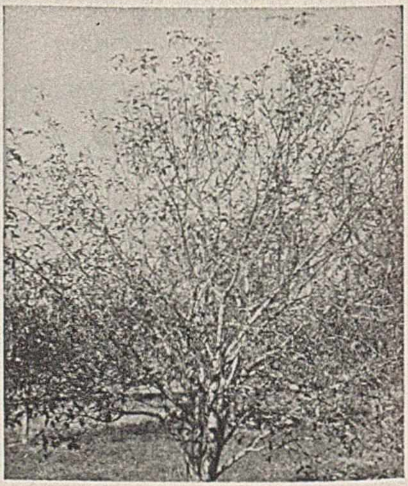
(Left) Tree on Which Copper Ammonium Silicate–Lead Arsenate–Orthol-K Spray Program Was Used



(Right) Tree on Which Bordeaux–Lead Arsenate Spray Program Was Used

(See page 287)

FUNGICIDE ADJUSTMENT

Preparation to Meet Requirements of Disease and Host

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Research Department, Watsonville, Calif.

Some fundamental conceptions of the mechanism by which fungicides manifest their toxic properties toward the fungus and the higher plant are presented. Commonly observed facts and some direct and indirect experimental evidence are brought forth to show that the acidity of the cell fluids and the precipitation of the protoplasm are seemingly closely related to the effectiveness of the fungicide toward the fungi and its safety toward the host. By considering these relationships as fundamental and sound, a new copper fungicide has been developed in which the activity may be adjusted to meet the requirements of the disease and host.

MATERIALS which possess high fungicidal properties are too often destructive to the host plants to which they are applied. Little difficulty has been experienced in selecting or devising compositions possessing fungicidal properties. The real problem has arisen in an attempt to retain a high degree of potency and at the same time to avoid undue injury to the fruit and foliage treated. The selecting or developing of compositions for the control of fungi has, therefore, come to be an ever increasing series of compromises in an attempt to arrive at a composition which will combine the maximum of destruction with the minimum of damage to the host.

Obviously the fundamentals of fungicidal development should be grounded in a clear understanding of the mechanism through which these compositions manifest their toxic properties toward fungi and the host plants, but actually little is known about this all-important foundation.

The questions constantly confronting workers in this field are: How do these fungicides work? What is the explanation for the differences constantly being manifested by copper and sulfur, the active principles of our most common fungicides? Specifically, why are copper fungicides effective in controlling diseases such as blotch, bitter rot, and fruit spot of apples, while sulfur is not? On the other hand, why is sulfur effective against certain rusts and powdery mildews, while copper is not? Again, why are copper sprays destructive to peach foliage, yet noninjurious to potato and bean plants, while sulfur sprays are unusually toxic to potato and bean plants but may be used with comparative safety on peaches?

In the complete answers to these questions lie the very fundamentals of disease control, which would greatly facilitate the development of new and more effective fungicides.

Action of Commercial Fungicides

Most of our commercial fungicides are characterized by a heavy metal or some acid-forming group. The heavy metal group is represented by the numerous insoluble copper compounds; the acid group is represented by sulfur. The toxic properties of sulfur are attributed to the various acids or acid-forming compounds produced when the sulfur is oxidized upon the surface of the leaf or adjacent to the fungous spore. These two types of chemicals—i. e., heavy metals and acids—are commonly used as protein precipitants in biological studies. It is by no means improbable that the toxic action of our common fungicides toward the fungus and the host plant is linked in no small way to their protein-precipitating power.

Soluble sulfur or soluble copper compounds are extremely toxic to higher plant life. To alleviate this toxicity toward the host plant, these fungicides are employed in a highly insoluble form. To become active, however, the fungicides, or products formed from their decomposition, must become more or less soluble. Just how, in the case of the insoluble copper fungicides, for example, the copper becomes effective is not thoroughly understood. Since, however, nothing can pass in or out of a living cell except it be in solution, it is obviously only the soluble copper, however slight it may be, that kills the fungus or injures the leaf cell. It is highly possible, then, that through the combined action of the plant, the spore, and the meteorological forces, copper is brought into solution and diffuses into the germ tube or leaf cell, causing coagulation or precipitation of the protoplasm and thus death to the fungous spore or host cell.

The destructive action of sulfur may also be a protein-precipitation process, since the action of acids on protoplasm is that of coagulation.

If, for example, a plant, the cell contents or cell membrane of which was acid or which secreted an acidic substance, were sprayed with an insoluble copper fungicide, it would be expected that this acid might bring a portion of the copper into solution, penetrate the cell, and precipitate the protein. If, however, a plant with cell fluids approaching neutrality were sprayed, the copper might be expected to remain in an insoluble, nondiffusible form and thus be harmless to the cell.

More specifically, if a copper oxide particle were applied to the surface of a cell which was acid, some of the copper might be brought into solution, enter the cell, precipitate the protein, and cause death. If, however, the cell content were near the neutral point, the copper oxide might remain in an insoluble, nondiffusible form which could not penetrate the cell, and thus no injury would occur.

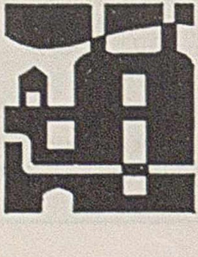
Let us now consider, according to the reasoning presented, the action of a sulfur spray on the first type of plant (acid type). We would expect, if the reasoning is correct, that little or no injury would occur, since the isoelectric or precipitation point of the protein of such a plant would undoubtedly be at a relatively low pH (acid), and thus the concentration of the acid formed from the oxidation of the sulfur might be insufficient to precipitate the acid protein. If, however, the sulfur were applied to the plant with a cell content approaching the neutral point, then a very small amount of acid from the oxidized sulfur might be sufficient to increase the acidity to a point where this particular protein would be precipitated. For example, let us assume that the acidity from sulfur accumulates until it reaches a hydrogen-ion concentration of pH 5. If the cell, or its contents, has a pH of 4 to 5, the isoelectric point of the protein will probably be at a lower pH than 4.5 and no injury will result; but if the protoplasm has a pH of 5.5 to 6, the acid from the sulfur may exceed the isoelectric or precipitation point of the protein and thus injure or kill the cell. This will apply whether the cell is the germ tube of a fungous spore or the epidermal cell of a leaf.

Ideal Fungicide

The ideal fungicide, in so far as safety to the host plant is concerned, would be highly buffered at the same pH as that of the cell fluids. Whether such a fungicide would be effective against the disease would depend upon the pH and isoelectric point of the germ tube of the fungous spore.

One may at first be inclined to question the importance of the pH and precipitation point of the protoplasm to the activity of the fungicide, for age and vigor of the host, nature of the protective tissue of fruit and foliage, as well as meteorological conditions, are all directly or indirectly related to the safety of a fungicide. Also, fungicidal efficiency is related to the type of fungus producing the disease, as well as the stage of its development. As we study these problems, however, in the light of the above ideas, we are led to wonder if these external factors, so well known to all, are not manifesting themselves because they are in some way altering the pH of the system, thus increasing or decreasing the activity of the fungicide or the sensitivity of the protoplasm. There are many indications that this is the case. Let us examine a few of these indications.

According to the above theory, potato and bean plants which are readily injured with sulfur but are very resistant to copper injury, should have a less acid protoplasm than peach foliage which is very sensitive to copper sprays and more resistant to sulfur sprays. Apples, on the other hand, which seem to be intermediate in their resistance to copper and sulfur sprays, might be expected to have an intermediate pH. It was interesting to find that the pH of the leaf tissue of beans and potatoes is higher (more alkaline) than most of our common plants, and that peach leaves are fairly acid. However, the pH of the apple leaves tested falls midway between the pH of the potato and the peach. In other words, the pH of these plants was found to agree with the above reasoning. The hydrogen-ion concentrations of the leaf tissues of these plants are as follows:



Expressed Fluid[a]	pH	Sensitive to S	Sensitive to Cu
Potato leaves	6.4	Yes	No
Bean leaves	6.0	Yes	No
Apple leaves	5.2	Medium	Fairly
Peach leaves	4.0	No	Highly

[a] These determinations were made in the fall of 1930. The potato and bean leaves were taken from young plants; the peach and apple leaves were fairly mature.

These data seem to show that the pH of the expressed plant fluids are closely correlated with the sensitivity of the plant toward fungicidal sprays.

In this connection, the meteorological conditions which lead to copper injury—i. e., cloudy humid weather—also favor increased acidity in plant fluids. Sulfur injury, however, is encouraged by hot, dry weather which hastens oxidation of the sulfur and decreases sap acidity.[1]

These data are in agreement with the reasoning presented; by considering these ideas as sound, a new commercial fungicide has been developed which presents some interesting possibilities.

In order that fungicides may be maintained on the plants at concentrations such as to be phytonomic to the host, yet to provide sufficient coverage to be effective against an invading disease, it is the practice, as previously stated, to employ fungicides which are insoluble in water. The common copper fungicide sprays and dusts used for plants in foliage have been the oxides, hydroxides, basic copper sulfates, carbonates, sulfides, etc., which are normally highly insoluble. It has too often been the case, however, that, when these normally insoluble copper compounds are subjected to atmospheric agencies and to the chemical action of materials accumulating at the leaf surface, the copper carried is brought into solution in sufficient amounts to become highly injurious to both fruit and foliage. It is probable, as previously stated, that the formation of various acids is responsible for the increased solubility of these copper compounds. To alleviate somewhat the danger from such copper injury, it has become general practice to employ an excess of lime (calcium hydroxide) in copper sprays. Bordeaux mixture is the most commonly used copper fungicide and is made by the addition of calcium hydrate to a copper sulfate solution. With the hope of improving the safety of this mixture, a large excess of lime is employed; for, although 1 pound of calcium hydrate will precipitate the copper in about 3.5 pounds of copper sulfate, in practice it is not uncommon for the user to employ nine to ten times this quantity of lime. The excess lime is apparently effective for a short time in preventing injury. It is also probable that for a time it decreases the fungicidal efficiency of the copper. Experiments and experience, however, have shown that the lime, spread out in a thin film on the surface of the leaf, forms a carbonate very rapidly; and as the carbonate forms, the copper becomes more available and more toxic to the host. These reactions by no means proceed at a constant rate. In fact, at no time can one determine or predict the point at which optimum fungicidal efficiency is properly balanced with optimum safety; and if it were possible to determine this fact, there is no known way to stop the reaction and hold it at this optimum point.

When the injurious action and comparative effectiveness of fungicides are considered in the light of the discussion

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[1] Ingalls, R. A., and Shive, J. W., *Plant Physiol.*, 6, 103-26 (1931); Rogers, C. H., and Shive, J. W., *Ibid.*, 7, 227-52 (1932).

presented, it appears that the logical procedure in producing a safe and effective copper fungicide would be to link the copper ion with a negative radical in such a manner as not only to render the copper insoluble but also to give the complex sufficient buffering power to stabilize the pH of the system at a point where the copper would exhibit maximum fungicidal efficiency and minimum injury to fruit and foliage.

Development of New Fungicide

In an effort to obtain a copper fungicide possessing these characteristics, numerous copper compounds were prepared and tested for their comparative safety and fungicidal efficiency. Some of the compounds studied which might be expected to possess some buffering powers were copper lignate, phosphate, resinate, proteinate, humate, oleate, bentonite, and silicate. Comparative laboratory and field tests showed that most of these compounds possess fungicidal properties, but all except the silicate were found too destructive to higher plants to warrant further development. Since these studies were made, however, copper phosphate has been prepared and used successfully by others.

The case of the copper silicate was interesting for, although it seemed to be somewhat lacking in fungicidal efficiency, it possessed the unique property of stabilizing the copper and thus rendering it entirely safe for use with the higher plants. In other words, the copper in this silicate was so insoluble and so completely buffered as to be relatively unaffected by the process which normally brings copper fungicides into solution. It was found that the buffering power of the complex could be decreased by the introduction of ammonia into the precipitating mixture.

With the introduction of ammonia into the system, which proved to be a simple procedure, the copper availability was increased, the proportion of silicate was decreased, the buffering power was lowered, and the fungicidal properties were improved. As was expected, concurrent with these adjustments the toxicity of the complex toward higher plants was increased. It was realized, however, that in this compound we had a fungicide in which the availability of the active principle could be so adjusted as to obtain maximum disease control with minimum injury to the host.

Determination of Adjustment Point

The problems were to determine just where this adjustment should rest. In other words, just how available or how highly buffered should this copper be to give maximum control with minimum injury. It was realized, however, that if the ideas presented above were correct, this "adjustment point" would not be the same for all plants or all diseases.

In solving this phase of the work, a group of compounds was prepared by employing different proportions of copper, ammonia, and silicate, which gave to the compounds different buffering powers or resistance to the influence of the various acids resulting from the action of the host plant and atmospheric agencies. The comparative buffering power, safety, and fungicidal efficiency of these combinations were studied in the laboratory and in the field, using numerous hosts attacked by several diseases. A few laboratory tests showing the close relation between the buffering power (denoted by resistance toward acids) of these "copper-ammonium silicates" complexes and their toxicity toward Pestalotia spores are presented in Table I.

The stability of the copper compound is measured by the amount of acid required to bring copper into solution. Had other fungous spores been employed, the actual percentage control by the various compositions might have been entirely different, although the order of ranking in comparative efficiency would probably have been the same.

TABLE I. BUFFERING POWER OR COPPER AVAILABILITY OF COPPER SILICATES AND THEIR EFFICIENCY IN CHECKING GERMINATION OF PESTALOTIA[a]

Sample No.	Na_2SiO_3–NH_4OH Ratio	0.1 *N* HCl	Cu Brought into Soln.	Germination of Pestalotia Spores Sprayed with 0.125% Insol. Cu[b]
			P. p. m.	
1	3–1	7	30	None
2	4–1	7	10	19.6
3	5–1	7	0	30.2
4	7–1	7	0	60.2
CuO	...	2	120	No test[c]

[a] One gram of sample was added to 50 cc. of distilled water, and the acid was added slowly under rapid agitation.

[b] Laboratory glass slide spore tests.

[c] On the checked or unsprayed slides, 92 to 97% germination occurred.

When 7 cc. of 0.1 *N* acid were added to the copper–ammonium silicate complex (sample 1) having a narrow silicate ammonium ratio, 30 parts per million of copper came into solution and the same amount of acid released only 10 parts per million in sample 2. Samples 3 and 4, with a high buffering power, yielded no soluble copper with this quantity of acid. Fairly large quantities of copper from black copper oxide, which possesses no buffering power, were released with only 2 cc. of the acid.

The data in the last column of Table I show that, when these copper compounds were applied as sprays to Pestalotia spores which had previously been placed on glass slides, the percentage of germination of the spores was apparently governed by the availability of the copper. In other words, where this amount of hydrochloric acid could not bring copper into solution, neither could the spores, and thus germination occurred. The amount of germination apparently was dependent upon the acid required to liberate the copper.

Comparisons were made of the relative toxicity of compounds, similar to those described, toward peach foliage. Peach trees were sprayed three times at weekly intervals, and all sprays carried 0.125 per cent copper which is equivalent to that in a 2–3–50 Bordeaux mixture. Leaf injury counts were made 2 weeks after the last spray application and are presented in Table II.

TABLE II. INJURY TO PEACH FOLIAGE FROM COPPER SPRAYS

Spray No.	Spray Material[a]	Defoliation or Leaf Drop	Leaves on Trees Showing Injury
		%	%
1	Bordeaux mixture 2–3–50 (2 lb. copper sulfate, 3 lb. lime, to 50 gal. spray)	95	97
2	Copper–ammonium silicate complex with buffering power slightly lower than that of sample 1 in Table I; approx. a (2–1) formula	90	92
3	Copper–ammonium silicate complex, approx. equivalent to a (4–1) formula or sample 2 in Table I	30	40
4	Same as spray No. 3, plus lime	25	30

[a] The copper concentration of all sprays and the lime in No. 4 are equivalent to that in the Bordeaux mixture.

It is evident from these data that the toxicity of these sprays to peach foliage is apparently closely correlated with the availability of the copper as measured by buffering power or the amount of acid required to bring the copper into solution.

The data obtained in determining the "optimum adjustment point" of these silicates for various diseases and hosts comprise thousands of fruit and foliage counts, and obviously cannot be fully presented in this report. Those interested in

Table III. Comparative Efficiency of Three Spray Programs in Control of Apple Diseases[a]

Fungicide	% Diseases, 1931 Apple scab	% Diseases, 1931 Fruit spot	% Diseases, 1931 Total	% Diseases, 1932 Apple scab	% Diseases, 1932 Fruit spot	% Diseases, 1932 Total	% Diseases, 1933 Apple scab	% Diseases, 1933 Fruit spot	% Diseases, 1933 Total	% Diseases, 1934 Apple scab	% Diseases, 1934 Fruit spot	% Diseases, 1934 Total
Sulfur program	11	60	66	9	22	28	12	33	40	2	..	2
Bordeaux program	..	..	..	8	3	11	14	3	16	2	..	2
Copper silicate program	5	4	8	5	1	6	2	6	8	1	..	1
Check (no sprays applied)	61	86	96	91	95	100	95	97	100	75	95[b]	75

[a] Courtesy of Department of Plant Pathology, New Jersey Agricultural Experiment Station.

[b] Fruit spot appeared only in the sulfur program.

these data may find some of them in the reports of the various eastern experiment stations where comparative field tests have been conducted. A summary of only a portion of the 4-year data on apple diseases from the Pathology Department of the New Jersey Agricultural Experiment Station are presented in Table III.

The fungicide used in the test presented in Table III was designated as (5-1), indicating that five parts of sodium silicate (N grade) to one part of commercial ammonia were employed in precipitating the copper from a copper sulfate solution. The data show that this composition possesses fungicidal properties toward apple diseases equal to that of other commercial fungicides. The investigation also showed that this product is less toxic to fruit and foliage than other copper sprays.

While this particular compound has proved its effectiveness as an apple spray under carefully controlled field tests and under commercial competition, other field tests have shown that, although it is entirely safe on potatoes, it lacks efficiency, and probably a more available formula would be much more effective as a potato spray and noninjurious to the potato foliage. It also appears that the melanose disease of citrus and rot of cranberries, for example, may require a compound with a higher availability in the copper and lower buffering power than do the common apple diseases.

This study is being continued with other hosts and diseases to determine where the compromise between safety and fungicidal efficiency lies, in order that a copper silicate composition may be prepared which will meet these requirements.

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OXIDATION OF FAT FRACTION OF ROASTED COFFEE

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THE purpose of this paper is to show that the fat fraction of roasted coffee undergoes chemical changes which indicate an oxidation when the coffee is packed in the presence of air or under such vacuum as can be provided in plant practice.

Inasmuch as the green coffee bean varies in chemical composition in accordance with species, source, and time of growth, and the roasted product derived therefrom may further vary according to the time and degree of the roast, great care was exercised in choosing the raw materials so that the results obtained would be directly comparable.

Preparation of Fat Fractions

For the first investigation a large batch of blended green coffee beans consisting of 40 per cent Brazilian Santos; 50 per cent Columbian Medellin, Bogota, and Bucaramanga; and 10 per cent Venezuelan Maracaibo species was used. One-third was set aside for a study of the green bean, and two-thirds were roasted. The color or degree of the roast was the standard used in the Boston area and, when measured with an Eimer and Amend reflection meter, gave a value of approximately 8.5 per cent. This percentage signifies the amount of light reflected from a surface of the ground coffee as compared with that reflected from a magnesium carbonate block. Using a roaster with 500 pounds (226.8 kg.) capacity, the roasting time was 20 minutes. The roasted beans were divided into two lots; one was set aside to age for 12 months in the bean form in ordinary paper sacks, and the other lot was ground and immediately subjected to extraction with redistilled petroleum ether. A large Soxhlet extractor capable of holding one pound (0.45 kg.) of ground coffee was used, and for the extraction of this amount of material, 1500 cc. of solvent were employed. All proceedings were carried out as closely alike as possible to avoid any discrepancies from this source. In the case of the green bean study, the beans were ground without previous drying and care was taken that the heat generated did not rise to a dangerous degree. The ground green beans were also placed immediately under petroleum ether which was the solvent to be used subsequently for the extraction of the fat, in order to avoid any fermentation. After aging, the stale roasted coffee beans were ground before extraction.

The extracts were dried over anhydrous sodium sulfate and under nitrogen, and the solvent was subsequently removed in an atmosphere of nitrogen at a maximum temperature of 60° C. with the help of a vacuum to remove the last traces of petroleum ether. The fats were then placed in a vacuum desiccator before analysis. To avoid ambiguity it may be stated that this fat fraction includes the substances which are extracted with petroleum ether and which remain completely soluble in the fat after removal of the extracting solvent.

In order to obtain the total yield of fat, a subsequent extraction was made of the coffees with redistilled ethyl ether after the constituents soluble in petroleum ether had been removed. The following table shows the percentage yields of the extracted fat with each of the solvents, calculated on the original and dried weights of the coffee:

Packed either in the presence of air or under a vacuum, roasted coffee and the fat fraction extracted from it with petroleum ether show definite undesirable changes in organoleptic tests upon aging.

An investigation of the fat fractions derived from fresh and aged roasted coffee obtained from the same lot of green coffee beans indicates that an oxidation takes place on aging. There is a slight fall in iodine value, a distinct rise in the Reichert-Wollny number, and a fall in the oxidizability value in the case of the fats from aged roast as compared with the values obtained on the fats from the fresh roast.

Roasted coffee which had been packed in vacuumized tins showed similar indications of oxidation on aging though in a less marked degree. A new modification of the Issoglio and the Kerr and Sorber method was developed for the determination of the oxidizability value with the use of potassium dichromate in place of potassium permanganate.

	Petroleum Ether		Ether		Total	
	Orig. Wt.	Dried Wt.	Orig. Wt.	Dried Wt.	Orig. Wt.	Dried Wt.
Green	10.75	11.94	2.50	2.77	13.25	14.71
Fresh roast	14.33	14.56	1.52	1.54	15.85	16.10
Aged roast	12.96	13.78	2.06	2.19	15.02	15.97

Since it has been reported by some investigators that fat is formed while others claim that much fat is decomposed in the roasting process (*9*), it is interesting to note that the 14.71 per cent fat yield from the green bean is equivalent to 16.10 per cent in the roasted bean when corrections are made for loss in weight due to the destructive distillation; therefore, no appreciable change in content of fat was found to take place in the roasting process.

Analysis of Fat Fractions

Only the fat extracted with petroleum ether was used in the work reported here, and reference will be made only to the fats derived from the fresh and aged roast. After removal of the acetone-insoluble phospholipids, the following constants were obtained:

	Freshly Roasted	Freshly Roasted, 6 Mo. Later	Aged Roasted
Iodine No. (Hanus)	96.05	95.00	95.65
Saponification No.	172.08	171.21	171.90
Reichert-Wollny No.	0.866	2.391	1.973
Sp. rotation in $CHCl_3$	...	−18.11°	−17.82°

Inspection of the Reichert-Wollny numbers shows that the value obtained with the fat from the freshly roasted is much less than that with the fat from the aged roasted coffee. Moreover, a large increase in this value was also obtained from the fresh fat after it had been standing for 6 months in a sealed bottle in a dark cupboard, as compared with the Reichert-Wollny number of the fat from the freshly roasted coffee.

The acetone-soluble fats were next saponified with 4 per cent alcoholic potash in order to separate the unsaponifiable matter from the saponifiable acids. A description of the unsaponifiable fraction has already been given by Bengis and Anderson (*1*), but it may be of interest to show two microphotographs of the most important constituent which was isolated and named "Kahweol," when crystallized from methanol and acetone (Figure 1).

The saponifiable fatty acids were then separated into their liquid and solid fractions by the methods of Gusserow (*7*) and Varrentrapp (*14*), and for the purpose of this paper only the liquid acids will be discussed. A complete description of the saponifiable acids was published in 1934 by Bengis and Anderson (*2*). It was found that these liquid acids were composed of oleic and linolic acids and an unsaturated, optically active, hydroxy acid which was insoluble in petroleum ether. After removal of this hydroxy acid by means of its insolubility in petroleum ether, an iodine number was determined on the mixture of oleic and linolic acids and the yields of each computed by the standard formula as given by Grün (*6*):

$$x + y = 100$$

$$\frac{89.93x}{100} + \frac{181.12y}{100} = I$$

The iodine numbers and yields of component liquid unsaturated acids are as follows:

	Freshly Roasted	Aged Roasted
Iodine No. (Hanus)	143.25	138.43
Linolic acid, %	58.47	53.18
Oleic acid, %	41.53	46.82

The iodine number of the fat from the aged roast is much lower than that obtained in the fat of the fresh roast and this fact indicates a rise in oleic acid and fall in linolic acid content due to oxidation. Where we have 58.47 per cent linolic acid and 41.53 per cent oleic acid in the unsaturated liquid acid fraction of fresh fat, the former drops to 53.18 per cent and the latter rises to 46.82 per cent in the same fraction of the fat from the aged roasted coffee.

Table I gives the detailed analyses of the fats extracted with petroleum ether calculated on a percentage basis. The analyses of the fats obtained by subsequent ethyl ether extraction are omitted.

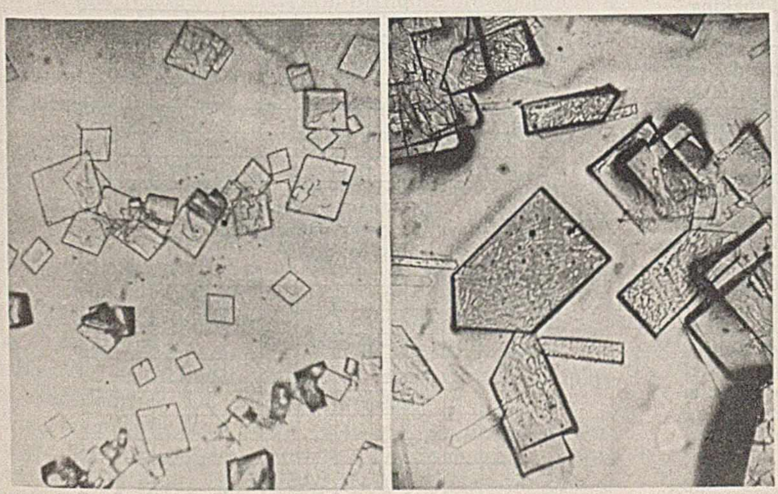

FIGURE 1. PHOTOMICROGRAPHS (× 55) OF KAHWEOL FROM METHANOL (*Left*) AND FROM ACETONE (*Right*)

TABLE I. ANALYSES OF FATS EXTRACTED WITH PETROLEUM ETHER

	Freshly Roasted	Aged Roasted
Total fat, %	90.4	8.63
Iodine No. (Hanus)	96.05	95.65
Saponification No.	172.08	171.90
Reichert-Wollny No.	0.866	1.973
Sp. rotation	...	−17.82°
Unsaponifiable matter, %	10.2	9.65
Saponifiable matter, %	87.0	86.75
Liquid acids	54.4	54.50
Linolic	29.5	27.00
Oleic	20.9	23.76
Petroleum-ether insol.	4.0	3.76
Solid acids	37.5	37.44
Lower acids	0.1	0.00
Palmitic	29.2	28.10
Stearic	6.4	7.40
Tetracosanic	1.8	1.90
Acetone-insol., %	0.08	0.21

Of especial interest in the subject of indications of oxidation is the Reichert-Wollny number which rose from 0.866 to 1.973, the linolic acid content which fell from 29.5 to 27.0 per cent, and the oleic acid content which increased from 20.9 to 23.8 per cent in the fresh and stale fat, respectively. In conjunction with these chemical findings the organoleptic tests should be mentioned. The fat extracted from the freshly roasted coffee possessed a most fragrant, full, and delectable aroma exactly like the coffee itself, and the flavor also had the same properties. The fat obtained from the aged roasted coffee was flat, musty, and rancid in aroma, and the flavor was unpleasant and irritating.

Modification of Issoglio Method for Oxidizability Value

In the second investigation a satisfactory method was sought for a direct quantitative measure of the extent of oxidation which could be performed on the extracted fat. Of all the methods inspected, the procedure for the determination of the oxidizability value, originating with Issoglio (*8*) and modified by Kerr and Sorber (*10*) was found to be the most expedient. Among others, the Kreis test in its various modifications and determination of peroxides was not at all satisfactory for use with coffee bean fat.

The Issoglio method was further modified in this laboratory in that potassium dichromate was used as the oxidizing agent in place of potassium permanganate. The former was found to give excellent results which could be checked with ease. The method as revised is as follows:

Ten grams of fat are weighed into a 200-cc. Erlenmeyer flask, treated with 100 cc. of distilled water, and heated on the steam bath under return condenser for 2 hours with occasional shaking. The suspension is cooled and treated with 5 cc. of 20 per cent sulfuric acid, and the fat is separated from the water extract by filtration through a thoroughly wetted, close-fitting filter paper. The filtrate is collected in a 110-cc. graduated flask and, after cooling, made up to the mark. After thoroughly shaking, a 10-cc. aliquot is taken for analysis and diluted with 50 cc. of distilled water. To the diluted aliquot 10 cc. of 20 per cent sulfuric acid are added and 25 cc. of 0.05 N potassium dichromate run in. The mixture is rapidly heated to boiling and boiled exactly 5 minutes under a return condenser which is connected to the 250-cc. Erlenmeyer flask by means of a ground joint. The flask is then immediately cooled to room temperature in an ice bath, treated with 10 cc. of 15 per cent potassium iodide solution, and titrated with 0.05 N sodium thiosulfate using starch as an indicator. The end point is very sharp since one drop of 0.05 N thiosulfate suffices to produce the color change. The oxidizability value representing the number of milligrams of oxygen required to oxidize the water-soluble constituents of 100 grams of fat is calculated by multiplying the difference obtained by subtracting the cubic centimeters of 0.05 N potassium dichromate required from that required in a blank, by 44, according to the following formula:

$$1 \text{ cc. } 0.05\ N\ K_2Cr_2O_7 = 0.4 \text{ mg. oxygen}$$

Let x = cc. of 0.05 N $K_2Cr_2O_7$ required for 10-cc. aliquot

then $$\frac{11x}{10} \times 100 \times 0.4 = \text{oxidizability value}$$

$$44x = \text{oxidizability value}$$

This method has proved eminently satisfactory and has shown evidence of oxidation in coffee long before the organoleptic tests. The method was applied to numerous samples of coffee and also coffee bean fats which had been kept under various conditions.

One series was carried out over a period of 12 months on a lot of roasted coffee which had been divided into five portions; four were packed under atmospheric conditions in tight glass jars, and the fifth portion was kept in a paper sack. The fat was isolated from all samples in identical manner and subjected to analysis for oxidizability value with the following results:

Age of Roast	Oxidizability Value
Fresh	141.0
10 days	102.4
20 days	94.5
4.5 months	78.3
12 months (open sack)	32.2

These values indicate conclusively a continuous decrease in oxidizable substances upon aging of the coffee. This decrease is much more rapid during the first month than thereafter. From results obtained on vacuum-packed coffee, it appears that oxygen absorption takes place under these conditions as well, though in a less marked degree.

A can of vacuum-packed coffee was opened 9 months after roasting and packing, and immediately extracted with redistilled petroleum ether in order to obtain the fat fraction. An oxidizability value of 87.5 was obtained on this fat. From the same lot of vacuum-packed coffee, a can was opened 3 weeks after roasting and packing and was immediately extracted. The fat was then allowed to stand in a glass-stoppered bottle under carbon dioxide in the dark for about 8 months. An analysis made for the oxidizability value showed a value of 96.3, or 8.8 mg. of oxygen more than was necessary for the unisolated fat. This finding indicates that conditions for oxidation seem to be better *in situ*, even though packed in vacuum, than in the isolated fat kept under carbon dioxide in glass in the dark.

Experiments on Vacuum-Packed Coffee

In order to arrive at more conclusive proof that coffee, packed under vacuum, undergoes oxidation, a series of experiments was inaugurated using a lot of coffee of which the

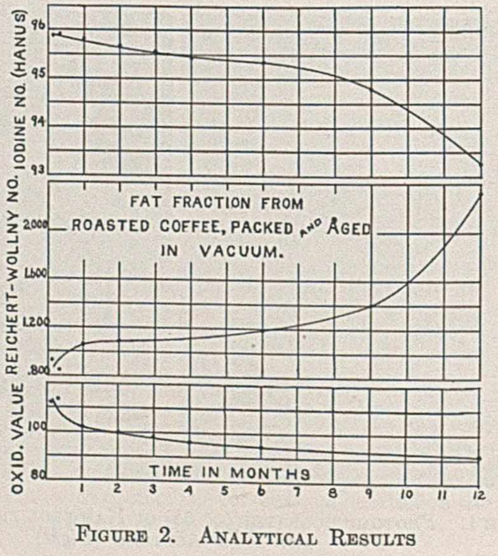

FIGURE 2. ANALYTICAL RESULTS

roasting date was known and which was packed in what is considered to be the highest type of vacuum package. Nine cans of this product were examined over a period of one year at various intervals.

All samples were extracted under identical conditions, and the fat was isolated with precautionary measures against oxidation by the use of nitrogen. Analyses were made immediately after isolation for the determination of iodine value, Reichert-Wollny number, and oxidizability value.

The first can was opened 4 days after roasting and packing, and showed a positive pressure. This was manifested by means of a manometer which was attached to the can in such a manner that the can could be punctured and the escaping gas directed against a mercury column. The evolution of gas from roasted coffee is very rapid at the start, and it is apparent that the vacuum is destroyed in a matter of hours after packing—that is, if the coffee was packed soon after roasting. The last can opened, which had been standing 12 months, showed a pressure of 368 mm. of mercury at 25° C. and at a barometer of 774 mm. This is equivalent to about 5.5 pounds above atmospheric pressure. The ends of the can were decidedly bulged.

Besides the analytical procedure, the aroma of the coffee and the aroma and flavor of the fat were observed. Table II gives the analytical results obtained.

Table II. Constants of Roasted Coffee Bean Fat

(All coffee from one lot packed in special vacuum cans)

Age	Iodine No.	Reichert-Wollny No.	Oxidizability Value
4 days	95.87	0.925	111.8
10 days	95.91	0.845	113.5
1 month	95.83	1.062	102.6
2 months	95.69	1.084	100.0
3 months	95.58	...	98.3
4 months	95.42	...	95.9
6 months	95.35	1.183	94.3
9 months	94.82	1.399	...
12 months	93.27	2.321	91.3

The iodine values fell from 95.9 to 93.3 with the age of coffee. The Reichert-Wollny values represent the volatile fatty acids; from 0.925 for the 4-day sample or 0.845 for the 10-day sample, the value increased to 2.321 for the 12-month sample. This value is considered a valuable indication of rancidity by many investigators in the study of fats. Just how high this value must be in the case of coffee bean oil to indicate undesirable rancidity is not exactly known. From this series, in conjunction with other observations, an arbitrary value of 1.25 might be acceptable. Scala (*13*), in his study of lard, olive oil, and residues of margarin manufacture considers a value of 2.0 as denoting absolute rancidity.

The oxidizability values given in Table II fall from about 112.6 to 91.3. Figure 2 gives graphic representations of these analytical results. There is no appreciable difference between the 4- and 10-day samples, but after that the changes cannot be denied.

With reference to the aroma of the coffee upon opening of the samples, the 4- and 10-day samples were very fragrant, rich, and full. The 1-month sample was still fragrant and rich but did not possess the fullness of the preceding samples. The 9-month sample showed a distinct stale and flat tendency, and the 12-month sample could not be mistaken in its possession of a stale, musty, and flat aroma. In other words, any semblance of rich coffee fragrance present in the early samples was almost entirely lost in the aged coffee.

The organoleptic tests of the extracted fats were found to run parallel to the findings on the coffee from which it was obtained. The first two samples had very fragrant odor and taste, whereas the 1-month sample lacked the fullness of the former. The 9-month sample was off in fragrance and had a tinge of rancidity, whereas the last sample derived from coffee 1 year old was even further off in fragrance and had a decided trace of rancidity.

Mechanism of Oxidation

The exact mechanism of this oxidation is difficult to explain. A few theories may be mentioned on the bases of work done by other investigators in other fields. The amount of flavor-bearing substance in coffee is small, perhaps only 0.0557 per cent as given by Erdmann (*3*). Therefore only slight changes may be necessary to develop a loss of flavor and aroma with a concomitant appearance of rancidity. Gröger (*5*) postulated that rancidity of fat is caused by hydrolytic action. There is about 2 per cent moisture in roasted coffee which makes this theory a possibility. Franke in 1932 (*4*) stated that several substances such as amino acids, carotinoids, and ergosterol, act as catalysts for autoxidation of oleic and linolic acid. Monaghan and Schmitt (*11*), in their work on autoxidation of unsaturated acids, state that oxidized carotene slightly accelerates it. Similar catalysts may well be present in the 10 per cent unsaponifiable matter which is contained in coffee bean fat. The work of Oparin (*12*) of the University of Moscow on respiratory pigments and their significance in oxidation of protein bodies is of special interest. He showed that chlorogenic acid acts as a catalyst in the oxidation of cleavage products of protein and of protein itself in the presence or absence of oxygen, in his work on sunflower seed, *Helianthus annuus*. Roasted coffee contains about 3 per cent of this chlorogenic acid, and it is highly possible that this substance behaves in a similar manner in coffee.

In conclusion it should be emphasized that the initial decrease in content of oxygen within the container obtained by special vacuum pack does not inhibit chemical changes affecting the aroma and flavor from occurring in roasted coffee. The most that can be said is that such changes are retarded in comparison with the changes occurring in the presence of air.

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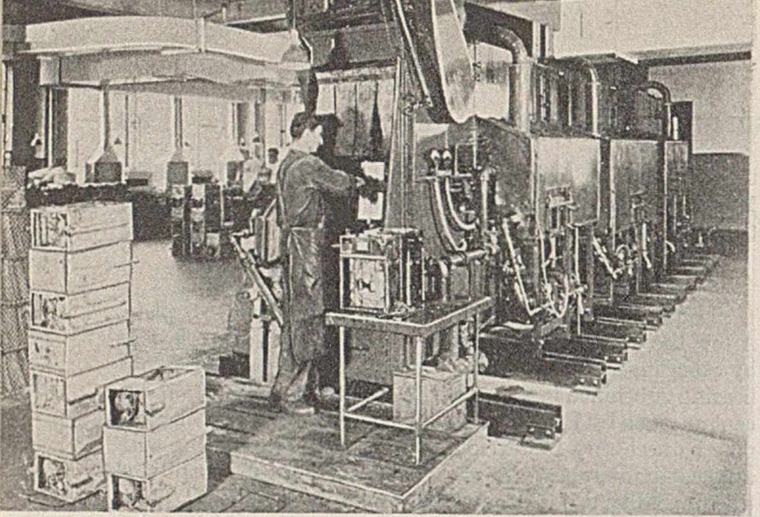

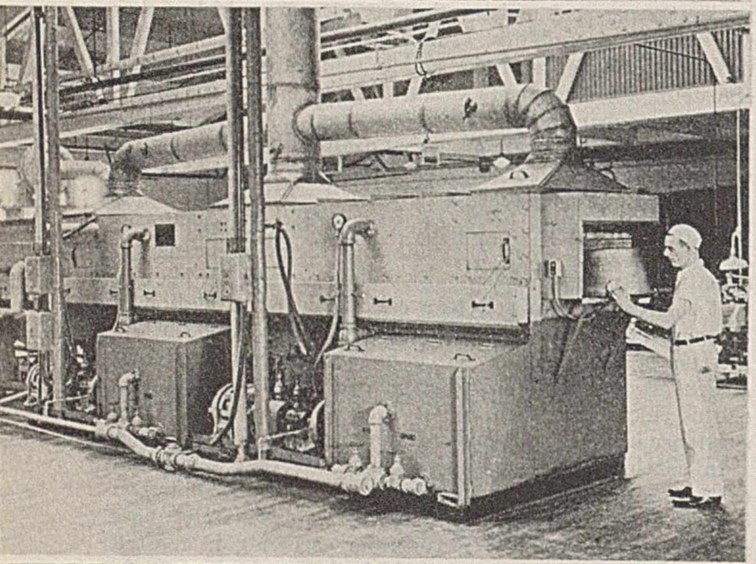

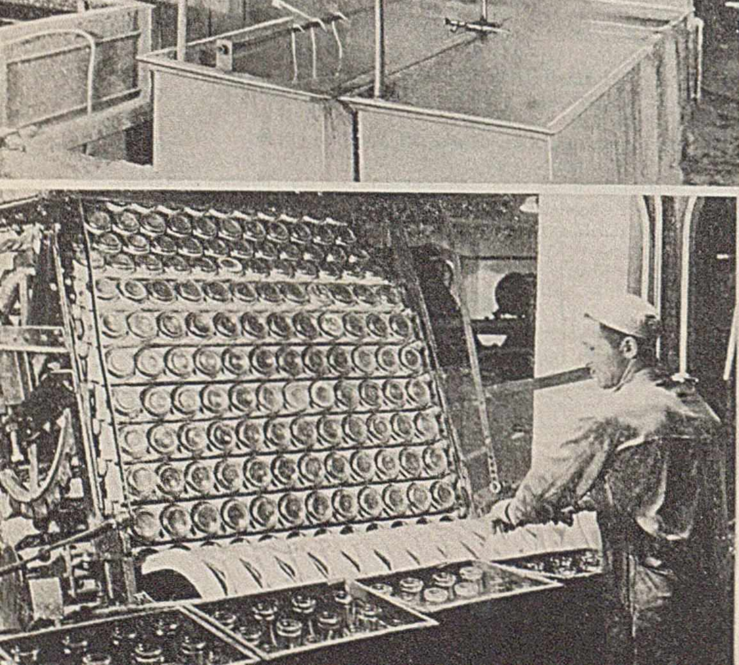

The Role of Silica —

Soluble Silicate Cleansers

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SILICATE solutions, either alone or combined with soaps, are used as cleansers in a great diversity of ways. Household and industrial uses are included. Compositions have been chosen partly on the basis of empirical trial and partly as a result of systematic study but, broadly speaking, the art of cleaning is not yet sufficiently understood to be called a science. Until this stage is reached, the attempt to evaluate particular reagents proceeds under a handicap. Cleansing is essentially complex because dirt is various and the surfaces from which it is to be removed are many and different.

The literature of the past decade has added to the knowledge of several phenomena which are important. The deflocculation of solid insoluble particles, the wetting of both solid and liquid surfaces, the effects of hydrogen-ion concentration, the appropriate amounts of alkali, and cost factors have all come in for a share of attention, and a partial basis has been laid for a more rational choice of detergents to fit particular needs.

The conventional view of soaps and alkaline compounds used for industrial cleaning has been to regard them as sodium or potassium salts without much emphasis on the effects contributed by the anions or the negatively charged colloidal micelles, as the case may be. Among the soluble silicates one hesitates to indicate the condition of the silica as silicate ion or colloid, although crystalline sodium metasilicate seems to be an orthodox chemical compound and solutions with four moles of silica to each mole of sodium oxide certainly contain colloidal matter. The lack of precise knowledge of constitution need not, however, prevent us from examining

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Reading from top to bottom—

WASHING GAS METERS RETURNED AFTER LONG SERVICE

WASHING BAKERY PANS WITH SILICATE SOLUTIONS

ELECTROCLEANING WITH THE HELP OF SILICATE

START OF MILK BOTTLES' JOURNEY THROUGH BATHS OF HIGHLY ALKALINE SILICATE the role of silica with respect to known attributes of detergents. Thus we may make useful comparisons among the different soluble silicates and between silicates and other inorganic salts.

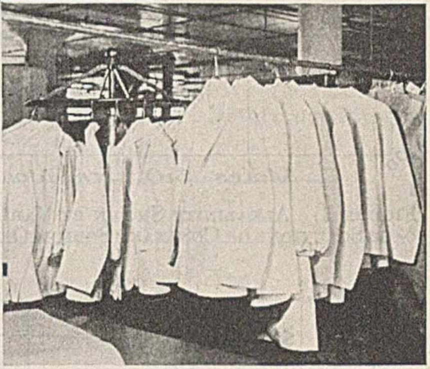
No attempt is here made to review all aspects of cleaning, even when they have been discussed in the literature, but rather to choose cases where the available data are sufficient to throw light on the influence of dissolved silica as a constituent of cleaning fluids. One result of the effort has been to indicate wide areas in which further work is needed. It is hoped that others may be interested to help supply the missing information.

Effect of Silica on pH

The curves of pH against concentration for silicates of varying alkali-silica ratio are asymptotic to a limiting pH for each ratio. The highest level reached by $Na_2O : 4SiO_2$ at any concentration is about 10.8, while metasilicate solutions reach pH 12 at less than 0.2 per cent. By plotting pH against ratio of sodium oxide to silica, a family of curves is obtained with constant sodium oxide; it appears, therefore, that the amount of silica associated with a unit of alkali has a material effect upon the intensity of its action and also that for a given pH which may be desirable for a particular kind of cleaning, varying amounts of alkali may be used within the family of soluble silicates (Figure 1).

Intensity of action is not completely indicated by hydrogen-ion concentration. The case is well illustrated by the behavior of alkaline cleaners toward tin and aluminum. Baker has studied a wide range of concentrations at 60° C. (*2*). From his data we can plot the concentrations of alkali as carbonate, phosphate, and silicate which are tolerated for 2 hours without etching tin plate (Figure 2). This figure shows that silica in solution exerts a protective action different from the phosphate and carbonate ions, and varying largely according to the relative amount of silica. The silicates provide safety for the metal at temperatures and concentrations of alkali effective for degreasing without the introduction of a poisonous inhibitor or an unstable reducing agent. The difference is clearly due to specific characteristics of the silica. Loss of weight from tin plate plotted against sodium oxide concentration shows the well-known fact that phosphate, carbonate, and metasilicate are less corrosive than equivalent normalities of hydroxide, that the different anions behave differently although all are able to cause injury to a tin surface in 24 hours at 60° C. (Figure 3). When, however, the data for silicates of higher ratio are put upon the same scale, we see the effect of silica which makes it possible to work safely with 1 per cent sodium oxide without appreciable loss using a 1:3 ratio, or to choose a lower ratio safely with less severe conditions of time or temperature (Figure 4). Such an operation as engineering a cleaning process for oily sardine tins can now be approached with something better than cut-and-try methods. Useful inferences can also be drawn by comparing these data with those of other workers who have found silicate solutions milder than other cleaners. For example, Zanker and Schnabel (*17*) showed that after two hundred cycles of boiling soap and soda, cotton fibers had lost 28 per cent of their initial strength, whereas in the presence of silicate of 1:2 ratio the loss was only 17 per cent.

(LEFT) SILICATED SUDS IN BLANKET WASHING



(RIGHT) WHITENESS PROTECTED WITH SOAP AND SILICATE

The polar ends of detergent molecules have perhaps had more than their share of attention. The anions of alkaline salts used in washing are here considered. Particularly, silica in cleaning solutions is shown to impart effects different from other anions, and differences between the soluble silicates are shown as functions of the alkali-silica ratio between Na_2SiO_3 and $Na_2O:4SiO_2$. Data from the literature are recalculated to show the influence of silica on pH, corrosion of soft metals, deflocculation, and the building effect by which the sudsing power of soap is increased.

Effect on Metals

The dairy industry uses a large amount of aluminum equipment which must be scrupulously clean. Aluminum is sensitive to alkalies in varying degrees according to the acid radical. Figure 5 shows that at 60° C. and 24 hours' exposure metasilicate is safe up to a concentration of 1 per cent sodium oxide, whereas the same sodium oxide as caustic, carbonate, or phosphate is harmful. The time and temperature are arbitrary; less severe conditions than those chosen for the comparison are usually sufficient for cleaning. With increasing relative amounts of silica, still higher concentrations of sodium oxide become safe, or, when occasion requires, more severe conditions of time and temperature can be chosen (Figure 6).

Bactericidal Effect

Hall (*7*) found that metasilicate solutions have a greater bactericidal effect than other sodium salts. All the salts investigated increased the ability of caustic solutions to destroy bacteria. Of these the silicate was most effective. Again silica appears to have a specific character and function though its action has not been explained.

Deflocculation

Most cleaning operations involve disposal of solid dirt which cannot be dissolved. Suspension in a liquid which is drained away and subsequent rinsing without redeposition

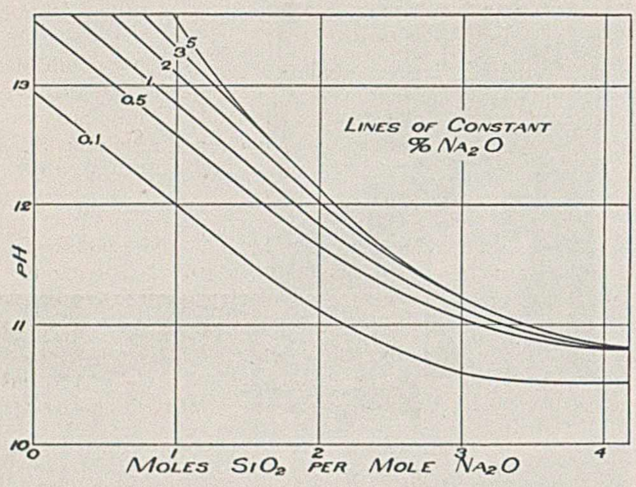


Figure 1. Alkalinity Shown by Variation of pH in Silicate Solutions of Constant Sodium Oxide Concentration

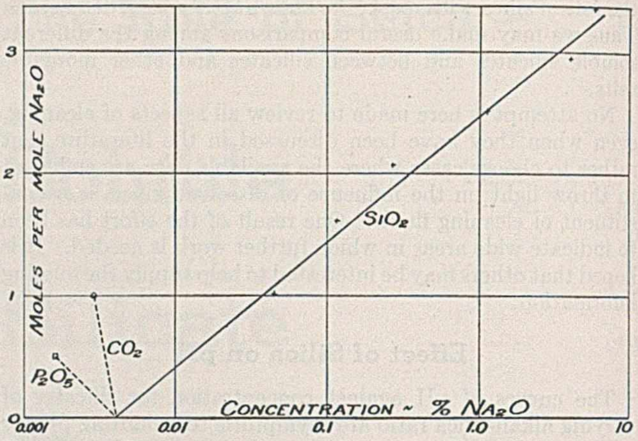


Figure 2. Protective Action Shown by Concentration of Sodium Oxide Tolerated by Tin Plate for 2 Hours at 60° C. without Etching (Recalculated from Baker)

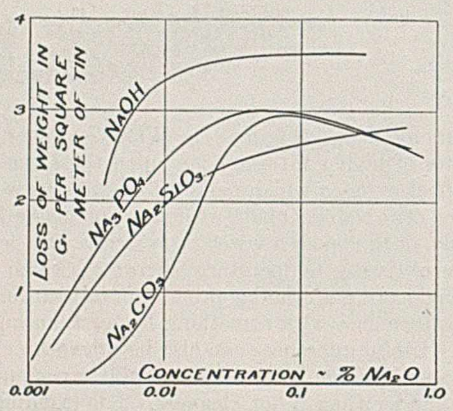


Figure 3. Protective Action Shown by Concentration of Sodium Oxide *vs.* Loss of Weight of Tin When Sodium Oxide Is Combined with Various Anions (from Data by Baker)

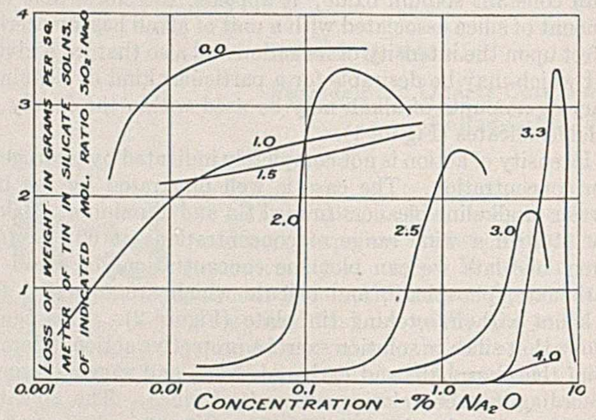


Figure 4. Protective Action Shown by Concentration of Sodium Oxide *vs.* Loss of Weight of Tin in 24 Hours at 60° C. When Sodium Oxide Is Combined with Varying Amounts of Silica (from Data by Baker)

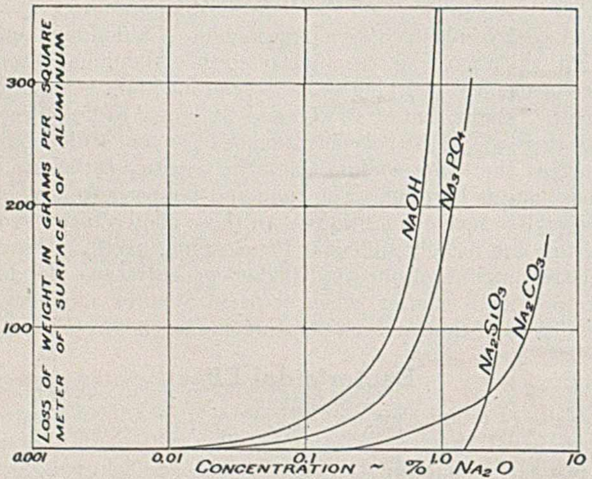


Figure 5. Protective Action Shown by Concentration of Sodium Oxide *vs.* Loss of Weight of Aluminum When Various Anions Are Present (from Data by Baker)

comprise the ideal process of removal. Silicate solutions are good deflocculators. McDowell (*9*) studied the dispersion of clay with silicates from the point of view of the ceramic industries, but his data can be rearranged to show effects of silica. By plotting viscosity of clay suspensions against ratio of sodium oxide to silica in the silicate, a family of curves of constant sodium oxide concentration is obtained which shows that the viscosity of a suspension of Tennessee ball clay is sharply reduced by increase of the silica ratio while alkali remains unchanged (Figure 7). Viscosity is a sensitive index of deflocculation; it bears a direct relation to the ability of the particles to resist the tendency to settle out of a fluid medium.

Another series carried out with Florida kaolin shows that a unit of alkali is most effective as $Na_2O:4SiO_2$, while combined as hydroxide or carbonate the smaller amount of deflocculation is striking (Figure 8). Fall (*5*) worked with finely divided manganese dioxide. His results also are susceptible to reëxpression to bring out the action of silica. His concentrations were nearer those likely to be encountered in laundry practice. A plot of his values for amount of solid suspended *vs.* percentage of silica in solution at temperatures of 40° and 75° C. for three alkali-silica ratios shows that the more siliceous solution suspends more dirt over a wider range of concentration than the more alkaline solution (Figure 9).

From Fall also we can take the suspending power of sodium as a base and plot the differences in results with like amounts of titratable sodium oxide in other combinations, which gives clear indication of the specific effect of silica in this aspect of the cleansing process (Figure 10). The range of concentration over which the silicate solutions exert good deflocculating action in comparison with the same amounts of titratable sodium oxide in other combinations is indicated in Figure 11.

Redeposition of Dirt

The redeposition of solid dirt of various kinds has been studied by Carter (*4*). It is well known to laundrymen and housewives that clean and heavily soiled fabrics must not be washed together lest dirt lifted from one be deposited on the other. This action is different from deflocculation. The silicates protect against redeposition, apparently as a function of the silica. The solutions higher in silica ratio gave whiter fabrics when exposed to most varieties of solid dirt. Caustic and carbonated alkalies have no ability to prevent redeposition under the conditions studied, and phosphates much less than silicates.

The mechanism of silica behavior in this respect has not been adequately explained, but this does not prevent the use of its peculiar properties in washing practice. This factor is one of the reasons for consistently better color in commercial laundering in the presence of soluble silicate.

Bleaching

The behavior of silicate solutions with peroxides in bleaching is unique. The silica in solution prevents loss of oxygen from alkaline baths which would otherwise rapidly depreciate. Though unexplained, the action is not that of alkali but of silica (for example, see citation *16*).

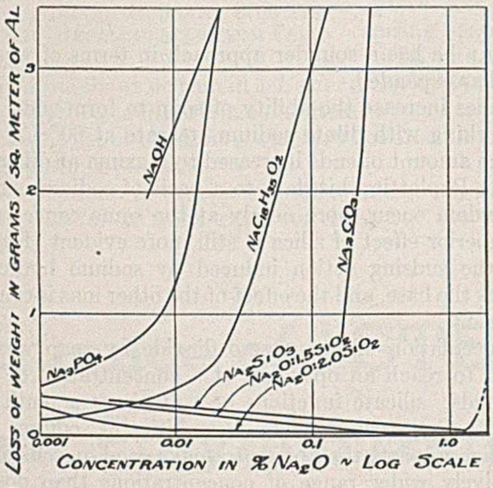


Figure 6. Protective Action Shown as in Figure 5 with Loss-of-Weight Scale Expanded One Hundred Fold

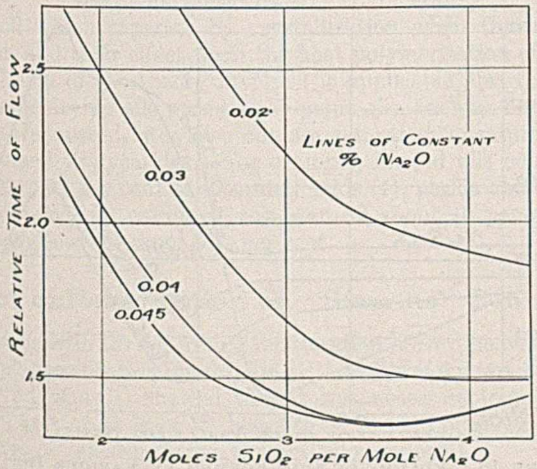


Figure 7. Deflocculation of Tennessee Ball Clay (Recalculated from McDowell)

Hypochlorite bleaching of cotton in the presence of silicate is less subject to iron stains and yields better colors with less danger of strength losses in laundering (*3*). These observations also rest on the properties of silica in soluble form.

Wetting Power

Silicate solutions have good wetting power against oils, including those free from saponifiable matter (*1*, *14*), against glass (*1*), and many metals (*11*). Comparison of the behavior of caustic solutions and silicate solutions used for washing milk bottles or for removing mayonnaise from glass leaves no doubt that the presence of silica improves the result, but the data are not available to give satisfactory quantitative

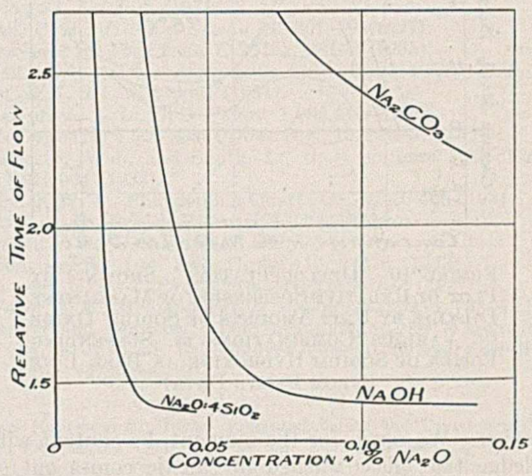


Figure 8. Deflocculation of Florida Kaolin, with Sodium Oxide as Carbonate, Caustic, and Silicate, *vs.* Viscosity (Recalculated from McDowell)

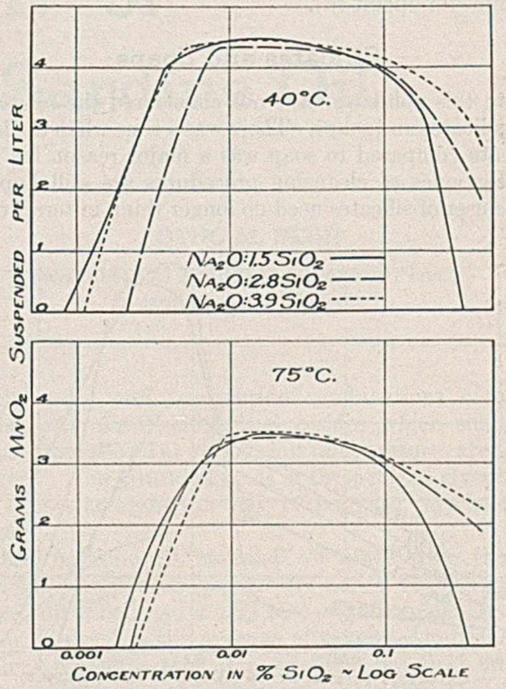


Figure 9. Deflocculation of Manganese Dioxide (from Fall's Data) *vs.* Silica Concentration for Three Silicates

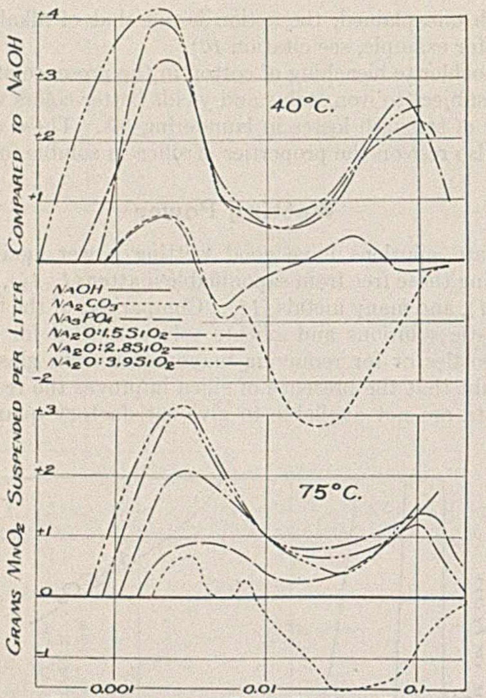


FIGURE 10. DEFLOCCULATION SHOWN BY PLOT OF RELATIVE SUSPENSION OF MANGANESE DIOXIDE BY UNIT AMOUNTS OF SODIUM OXIDE IN VARIOUS COMBINATIONS *vs.* SUSPENDING POWER OF SODIUM HYDROXIDE AS BASE LINE (FROM FALL'S DATA)

expression. We must, for the moment, be content with the knowledge that glass washed in caustic comes out of the rinse with standing drops of water, whereas with silicate the water flows out into an even film. Wetting power of silicate solutions against oil and glass has been shown by the work of Baker (*1*) and Peterkin (*10*). Grayson has discussed the use of silicate solutions in dairy cleaning from a practical and economic standpoint (*6*).

Silicates and Soaps

Up to this point we have not considered the relations between silicates and soaps. There was a time when the low cost of silicate compared to soap was a major reason for its use. The economies of cleansing procedures are still important, but the user of silicates need no longer think in terms of adulteration; he has a sounder approach in terms of work done per dollar expended.

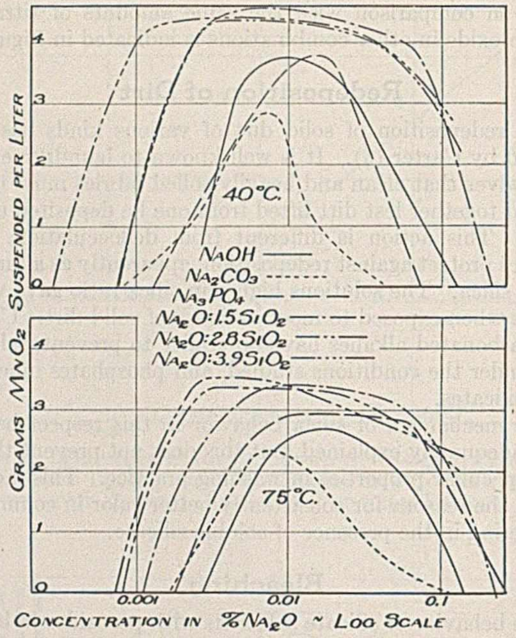


FIGURE 11. DEFLOCCULATION AS INDICATED BY THE SUSPENDING POWER OF SODIUM OXIDE IN VARIOUS COMBINATIONS, SHOWING THE EFFECT OF SILICA ON AMOUNT AND RANGE

Alkalies increase the ability of soap to form suds. Baker (*1*), working with dilute sodium stearate at 60° C., showed that the amount of suds increased to maxima at different pH values. Replotting his data to a basis of sodium normality, the maxima occur more nearly at the same concentrations. The superior effect of silica is still more evident (Figure 12) when the sudsing action induced by sodium hydroxide is taken as the base, and the effect of the other ions is considered (Figure 13).

Deflocculation of manganese dioxide by soap was found by Fall to reach an optimum at a concentration of 0.2 per cent solids; silicate functions best at about a tenth of this amount. Comparing similar normalities of sodium, we find that silica imparts the ability to make good suspensions over a relatively wider range of concentrations than does soap (Figure 14). Silicated soaps thus give not only more suspending power per unit of cost, but greater protection against unfavorable conditions.

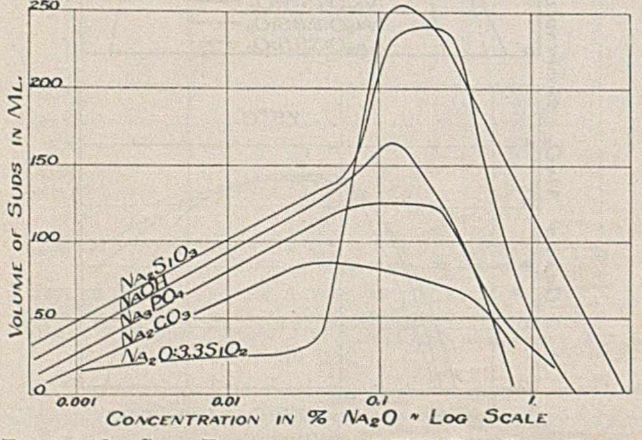


FIGURE 12. SUDS FORMED ON AN 0.0088 PER CENT SODIUM STEARATE SOLUTION *vs.* UNITS OF ALKALI, SHOWING ANION EFFECTS (RECALCULATED FROM BAKER)

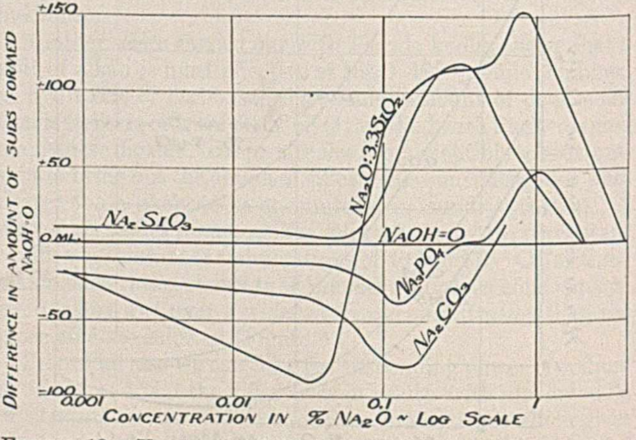


FIGURE 13. VOLUME OF SUDS FORMED BY VARIOUS BUILDERS PLOTTED WITH THE AMOUNT OF SUDS FORMED BY CAUSTIC AS A BASE LINE (BAKER'S DATA)

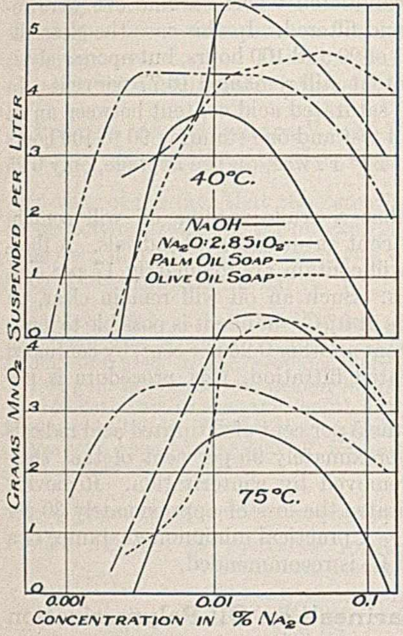


Figure 14. Deflocculation as Shown by Concentration of Sodium Oxide *vs.* Suspending Power on Manganese Dioxide at 40° and 75° C. When Sodium Oxide Is Combined as Soaps, Silicate, and Caustic (Recalculated from Fall)

Soap and silicate mixtures (*1, 14, 15*) are good emulsifiers. Qualitative observation of such processes as making asphalt emulsions (*8, 12, 13*) leads to the impression that soluble silica contributes to the results obtained. Here again is a field for further study.

Under the conditions here reviewed the silica is in solution and can readily be rinsed away after its work is done. Laundries often find it possible to rinse less when using soap built with metasilicate, and fabric shows no gain in ash after many cycles. Contrary results reported in certain older literature can only have come from the use of conditions which do not arise in modern American washing practice.

Silicate solutions in washing practice, then, are alkaline compounds useful in some cases as such, but more often exhibiting distinctive properties as a function of the silica they contain. The freedom from stoichiometric boundaries within wide limits gives them a range of characteristics which further distinguish them from other alkalies used in cleansing processes.

In the interest of brevity, no attempt has been made to point out all the relationships to be derived from the graphs. They summarize extensive data and contain evidences worth careful study by those interested in detergent technic. Much additional work is needed to comprehend adequately the mechanism of cleaning in general, and in particular the advantages to be gained from the use of soluble silicates.

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Influence of "STEARINE" on Heat Polymerization of Sardine Oil

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THIS paper deals primarily with the "stearines" (the higher melting mixed, saturated, and unsaturated, triglycerides) of sardine oil which separate by crystallization when the oil is chilled, and their effect upon the heat polymerization of the oil. Much of the theory involved is applicable also to the vegetable drying oils because the paint oils, such as linseed, perilla, hempseed, etc., also contain saturated, unsaturated, and mixed triglycerides. For example, linseed oils contain from 6 to 11 per cent of saturated acids (*1*), perilla about 12 per cent (chiefly palmitic), soy-bean oil about 10 per cent, and hempseed oil about 9$^1/_2$ per cent.

Effect of Refrigeration on "Stearine" Content

In a bulletin (*3*) describing refrigeration of sardine oils and a simple specification for checking the degree of winterization, a curve (Figure 1) showed that it was necessary to specify a chill test of at least 12 hours to be assured of an oil that was free of "stearine" from a practical standpoint.

Fish-oil "stearine" is not accurately defined. Pure stearin is the triglyceride of stearic acid, but in commercial parlance the mono-, di-, and triglyceride combinations of mixed, saturated, and unsaturated triglycerides which solidify or crystallize from the oil at various low temperatures are termed "stearines." The saturated acids in these mixed glycerides of sardine oil are composed mostly of palmitic, myristic, and stearic acids.

Weighed portions of "stearine" obtained from the filter press in the refrigeration plant were added to a thoroughly winterized oil which had a chill test of 41 hours. The curve shown in Figure 1 is the average of several determinations. This curve indicates that it is of little practical value to winterize an oil to stand up beyond a standard chill test of 12 hours, but that it is vitally important to clear the oil of "stearine" to this extent. Based on these data, this company

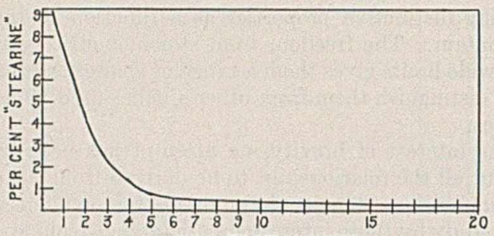

Figure 1. Relation between "Stearine" Content of the Oil and Chill Test

decided to have its winterized oils stand, on the average, 15 or 16 hours.

However, a fully refined sardine oil, standing a chill test of 40 hours, with an iodine value of 203.45, analyzed by the Twitchell (*2*) lead salt–alcohol precedure, was found still to contain 17.5 per cent saturated acids. (The experimental error in a single saturated acid determination may be as high as 0.5 per cent.)

It was decided, therefore, to determine the relation between the chill test and the actual percentage of saturated acids in the oil. Figure 2 represents the results. This curve is also asymptotic and, allowing for normal experimental errors in the saturated acid determinations, it substantiates the previous conclusion—namely, that an oil standing 15 or 16 hours is practically free of these glycerides containing saturated acids which will solidify at 32° F. (0° C.)

Chill Tests. The chill tests referred to in this paper were made according to a tentative specification for a standard chill test for sardine oils which is a modification, by the writer, of the standard cold test of the National Cottonseed Products Association. This test is easily made with simple equipment:

> Filter about 250 cc. of the oil to be tested into a suitable Pyrex beaker. Heat on the hot plate until the stirred oil registers 120° C. (248° F.). Transfer the oil, while still warm, into two standard 4-ounce (118.4-cc.) sample bottles. [This should be done at about 50° C. (122° F.).] Insert a cork stopper tightly and seal with paraffin. Attach a waterproof tag by wire to the neck of the bottle for sample identification.
>
> When the oil in the bottle is at room temperature (not to exceed 25° C.) note the date and time and bury the bottles completely in a bucket of finely cracked ice, and add sufficient cold water so that it rises in the bucket of ice to the top of the bottles. Replenish the ice when necessary to keep the bath at 0° C. Examine the oil for clarity and brilliancy at hourly intervals, and as soon as a cloud is observed in the oil, note the date and time on the tag.
>
> The time, in hours, from immersion of the sample in the cracked ice to the appearance of a cloud is the reported chill test.

Other chill tests which, for example, require an oil that will remain clear for 2 hours at 22° F. (−5.5° C.) are difficult to duplicate and require elaborate equipment. An oil which remained clear for 2 hours at 22° F. had a saturated acid content of 16.77 per cent. It appears, therefore, that oils refrigerated to stand clear for 2 hours at 22° F. will retain practically the same amount of saturated acids as those that pass the standard 20-hour chill test.

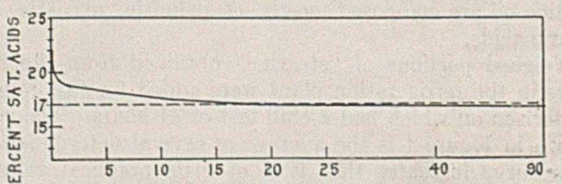

Figure 2. Relation between Actual Content of Saturated Acids in the Oil and Chill Test

Experiments were conducted where sardine oils were repeatedly refrigerated and filtered. In this case the clear oils would stand a chill test of 90 and 100 hours, but upon analysis the saturated acid content still remained 16.77 per cent. In short, the difference in saturated acid content between an oil standing a 20-hour chill test and one standing 90 to 100 hours at 32° F. or 2 hours at 22° F. was, on the average, only 0.25 per cent.

These tests show that a crude sardine oil will contain approximately 22 per cent saturated acid radicals. A thoroughly winterized oil will contain approximately 17 per cent saturated acid radicals. Such an oil will remain clear, on an average, for 20 hours at 0° C. While it is possible to lower the saturated acid content another 0.25 per cent, by continued refrigeration and repeated filtration, this procedure is impractical.

It is estimated that the 5 per cent of saturated acid radicals removed constitute approximately 95 per cent of the "stearine" which may be removed by winterization. Removing this 5 per cent necessitates the loss of approximately 30 per cent of the original oil. A practical minimum guarantee of a 14-hour chill test at 0° C. is recommended.

Influence of "Stearines" on Oil Polymerization

Theoretically, the presence in an oil of saturated acid radicals would hinder the polymerization of the oil. A varnish plant in the East, which uses a recording thermometer during the kettle-bodying of sardine oils, reported that a thoroughly winterized oil with a 12-hour chill test (F. F. acid, 0.25 per cent) polymerized several hours sooner, to the same degree of polymerization as measured by the viscosity, than winterized varnish-grade oil previously used. The only reasonable explanation was that the former oil was lightly winterized, in which case it would have a chill test of 0.5 to 0.75 hour. No sample remained for test purposes; therefore to prove this point, the following experiment was conducted:

> Two 20,000-pound (9000-kg.) batches of sardine oil were taken from the same tank and were alkali-refined, bleached, and filtered in the same manner. One batch (VMO6) was lightly winterized to stand a chill test of 0.5 hour. The other batch (VMO8) was "zerolized" and turned out with a chill test of 20 hours. In order, for comparison, to have a sample abnormally high in "stearine," a third sample (VMOO) was made up with "stearine" collected from the filter press during the first filtration. This sample had a saturated acid content of 27.7 per cent.
>
> These three oils were then heat-bodied at the same time, in the same oil bath, under identical heat input conditions, and for the same length of time. Roughly, the heating was carried to 500° F. (260° C.) in one hour, then to 565° F. (296° C.) in 0.5 hour, and finally held at 565° F. for 0.5 hour.

During the reaction the zerolized oil liberated the most heat during the exothermic reaction of polymerization, but, since this was allowed to escape, the temperatures of the oils remained within 5° F. (2.8° C.) of one another.

The results are as follows:

Oil	Viscosity *Decipoises*	Polymerization %	Iodine Value
VMO8	62.7 (U)[a]	70	125.6
VMO6	47 (R)	50	116
VMOO	30 (L)	15	103

[a] Letters in parentheses are Gardner-Holt viscosities.

The zerolized VMO8 oil acquired a body 133 per cent greater than the lightly winterized VMO6, but the actual percentage of oil polymerized, as measured by the insolubility of polymerized oil in acetone, was 140 per cent greater. The difference in the saturated acid content of the two winterized oils was only 2.5 per cent but this difference, measured as solid saturated acids, was 50 per cent.

It may be concluded, therefore, that highly refrigerated oils will polymerize more rapidly under the same heat input than lightly winterized oils. The presence of glycerides, solid at freezing temperatures, are detrimental to polymerization.

Influence of "Stearine" on Reactivity of Sardine Oil with Synthetic Resins

In view of the fact that the "stearines" have an influence on the polymerization of the oil itself, it was decided to determine their influence on the reactivity of the sardine oils with some of the synthetic resins:

Experiment 1. One hundred grams of a 100 per cent phenolic resin were heated with 200 grams each of three alkali-refined sardine oils used in the previous polymerization experiments. The oil-gum mixtures were heated in the same size flasks in the same oil bath and for the same length of time to insure equivalent heating conditions. The heating was carried to 565° F. (296° C.) in one hour, then held at 565° F. for one hour. The results are given in Table I.

Table I. Effect of "Stearine" on Reactivity of Oils with Synthetic Resins

Oil	Viscosity in Decipoises at 25° C.		
	Bakelite BR 254	Rauzene X150	Ester gum No. 1
	Experiment 1		
VMO8	155 (X-Y)[a]	..	..
VMO6	129 (X)	..	..
VMOO	77 (U-V)	..	..
	Experiment 2		
Solution only, VMO8	40 (P)	..	..
	Experiment 3		
WSO3	362 (Z2)	88 (V)	44 (Q)
	Experiment 4		
VM linseed oil	55 (T)	11 (D-E)	10 (D)

[a] The letters in parentheses are Gardner-Holdt viscosities.

The degree of reaction was to be judged by the resulting viscosities of the oil-resin mass. The body of the oil-resin reaction was so heavy, however, that it was found necessary to add 200 cc. of pure turpentine to each flask in order to obtain satisfactory viscosity readings. After the addition of 172 grams (200 cc.) of turpentine, the zerolized oil (VMO8) produced a viscosity 120 per cent greater than the lightly winterized oil (VMO6) and 200 per cent greater than the oil abnormally high in "stearine" (VMOO).

Experiment 2. To determine how much of this body was due to pure gum solution in the bodied oil, the zerolized oil was heat-bodied under the same temperature condition; to 200 grams of this oil, 100 grams of Bakelite BR 254 were added. The mixture was warmed sufficiently to dissolve the resin without reaction (300° F., or 148.9° C.) and reduced with 200 cc. of turpentine. The viscosity was 40 decipoises. Consequently, where the oil and resin were allowed to react at 565° F. (296° C.), the resulting body of the thinned varnish was practically 400 per cent greater than the body of the bodied oil with the resin dissolved therein.

The conclusion is that the zerolized oil (VMO8) reacts decidedly better with the 100 per cent phenolic resin than the lightly winterized oil (VMO6).

Experiment 3. To compare the reaction of phenolic resins, modified phenolic resins, and ester gum with sardine oil, experiment 1 was repeated. However, in this case the oil, a nonbreak zerolized sardine oil (WSO3) with an acid number of 1.5, was the same in the three beakers but the resins were changed; that is, 100 grams of ester gum No. 1, Rauzene X150, and Bakelite 254 were used with 200 grams of oil and subsequently reduced with 172 grams of turpentine. The results are given in Table I. The body of the ester gum–sardine oil reaction was about the same as the body of the purely dissolved resin (Bakelite 254) in the heat-bodied sardine oil, which would indicate that the ester gum–sardine oil mixture was merely one of solution. The Rauzene X150, after being reduced with thinner, was twice as heavy, and the Bakelite 254 about eight times as heavy in body as the ester gum–sardine oil mixture. Another interesting observation is that the neutral Varnish Makers sardine oil (VMO8), bodied in combination with Bakelite 254, had less than half the viscosity of the nonbreak sardine oil (WSO3) which had an acid number of 1.5.

Experiment 4. Experiment 3 was duplicated as nearly as possible, using a Varnish Makers linseed oil in place of the sardine oil. The nonbreak sardine oil (WSO3) produced with Bakelite 254 a varnish with a body nearly seven times as heavy as the Varnish Makers linseed oil; and the Varnish Makers sardine oil produced a body nearly three times as heavy as the Varnish Makers linseed oil.

In these experiments the heating curve of the oil bath did not vary over 10° F. (5.6° C.) during the 2 hours when the temperature of oil was above 450° F. (232.2° C.).

The conclusion is that more reaction takes place between phenolic resins and sardine oil than with linseed oil (probably because of the highly unsaturated clupanodonic acid radicals in the sardine oil) and that a maximum of reactivity takes place with thoroughly winterized oils. It would appear well worth while for the varnish maker to investigate the possibilities of varnishes made with synthetic resins in which the sardine oil would replace the linseed oil completely and part of the China wood oil.

Acknowledgment

The writer wishes to acknowledge with appreciation the work of Potter Holmes, who made the saturated acid determinations, and Thayer Pattison, who assisted with the laboratory work. The writer is also indebted to B. M. Pattison for permission to present this paper.

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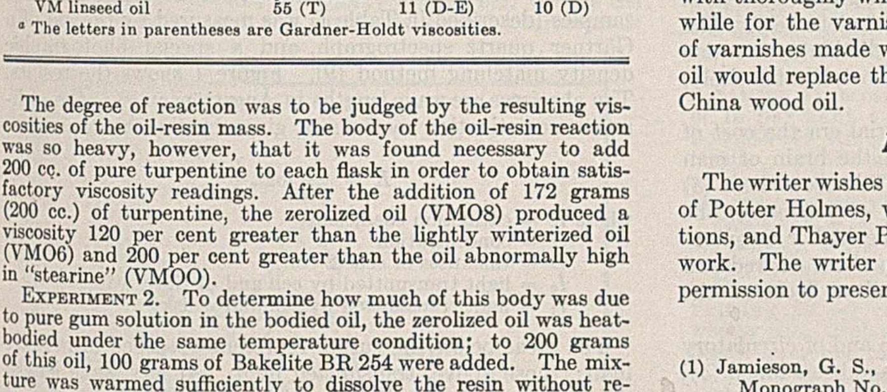

Bessemer Steel Plant, Pittsburgh, Pa.

From a painting reproduced by courtesy of School of Mineral Industries Gallery, The Pennsylvania State College

Changes in Whisky during Aging

Shown in the Ultraviolet Absorption Spectra

A preliminary study of the absorption of ultraviolet light by whisky was made. Seven samples of whiskies varying in quality from an aged 6-year-old rye bourbon to a blend of alcohol with 6-month-old whisky were studied. The results show that whisky gives a characteristic ultraviolet absorption spectrum and that aging apparently increases the absorption. A study of the spectra of all substances identified in whisky, together with the changes that occur over a period of years in storage, may lead to important developments in the manufacture and aging of whisky.

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PRIMITIVE man doubtless discovered that age improved the quality of wine during his efforts to preserve the beverage from one harvest to another. When the still was invented, it was found possible to secure a beverage of greatly increased potency which could be kept (if desired) indefinitely. The effect of age on the palatability of the distillate was also noted, and soon age and quality became almost, if not entirely, synonymous (*3*, *6*, *12*, *14*, *16*).

With the advent of the modern industrial era the cost of storage became of great importance and the brain of man tried to devise methods of quick aging. The use of heat (*8*) during storage was the obvious method of increasing the velocity of a reaction. Unfortunately the higher temperatures seemed to cause other changes than those desired and the palate, that supreme court of quality, declared the product unconstitutional.

The use of chips or sawdust (*10*, *11*, *15*) and of circulatory systems (*18*) has been tried; chemicals have been added (*5*); oxygen (*4*, *17*), ozone (*1*, *2*, *11*, *13*), and hydrogen (*11*) have been bubbled into the raw spirit; and electrolysis (*11*) has been used in an effort to speed the process. The final verdict has always been in favor of the naturally aged product. So firmly is this preference established that distillers of quality products regard all proposals for quick aging with indifference, if not with suspicion.

The reason for the failure to speed the process lies in the complexity of the changes that occur, and the author believes that, until a much more thorough understanding of the nature of these reactions is secured, such attempts are bound to fail. Better methods of analyses are needed as well as a more careful study of the individual reactions that take place.

TABLE I. CHEMICAL ANALYSIS OF WHISKIES (IN MG. PER 100 ML.)

Sample No.	Description	Residue	Acids as Acetic Fixed	Acids as Acetic Volatile	Esters	Aldehydes	Furfural	Higher Alcohols
I	5-yr. rye	162.0	37.8	31.2	58.0	6.0	3.0	137.2
II	5-yr. bourbon	173.0	39.6	28.8	60.5	6.6	2.5	141.9
III	6-yr. rye and bourbon	152.0	40.8	30.0	52.8	6.6	3.0	137.2
IV	15% 4-yr. and 6-mo. mixture	120.8	39.7	18.6	28.2	3.2	2.0	141.0
V	6-mo. straight	107.2	30.0	17.0	24.6	2.9	2.0	132.0
VI	20% 4-yr. and alcohol blend	170.0	16.5	10.8	22.8	1.7	0.5	75.0
VII	25% 6-mo. and alcohol blend	146.4	15.0	9.0	17.6	1.1	0.1	52.8

Measurement of Ultraviolet Absorption

As a contribution to this problem, a preliminary examination of the ultraviolet absorption spectra of various grades of whisky was made. The ultraviolet absorption of the samples (described in Table I) was measured by the aid of a Gärtner quartz spectrograph, and a special photographic density matching method (*9*). Figure 1 shows the results. The abscissas are wave lengths in Ångström units; the ordinates are extinction coefficients, given by the equation:

$$K = \frac{1}{CD}\log_{10}\frac{I_0}{I_1}$$

where K = extinction coefficient
C = concentration
D = thickness of cell (2 cm.)
I_0 = light transmitted by cell and distilled water
I_1 = light transmitted by cell and whisky

The areas below the curves represent absorbed ultraviolet light; those above, transmitted light. At any wave length the ability of the undiluted whisky to absorb light of that frequency is expressed by the value of K. The values of K are given in Table II.

A preliminary test showed that the undiluted whiskies absorb ultraviolet light so completely that measurements could not be made. Dilutions of 1 to 10, 1 to 25, and 1 to 50 were then made and photographed. The 1 to 10 dilution was still too concentrated for the entire curve to be obtained. The 1 to 50 was too dilute for accurate measurements. The 1 to 25 dilution was by far the most satisfactory, and the results can be regarded as sufficiently accurate to say that, in most regions, the differences in the curves are real and reproducible.

Notwithstanding the inaccuracy of the results obtained from the 1 to 10 and the 1 to 50 dilutions, Table III is given to confirm the relative orders of absorption. The regularity thus observed proves that the results obtained at a dilution of 1 to 25 are by no means fortuitous, but seem to represent a distinct change of absorption spectra with the age of the whisky. Blank spaces in Table III represent absorptions too large or too small to be determined at that wave length and dilution.

TABLE II. VALUES OF K USED IN FIGURE 1 (DILUTION 1 TO 25)

Sample No.	2300	2400	2500	2600	2700	2800	2900	3000	3100	3200	3300	3400
	Wave Length in Ångström Units											
I	..	25.0	17.9	17.3	19.5	20.5	16.2	12.0	9.3	7.7	6.2	4.1
II	..	20.5	16.0	15.8	17.9	18.8	15.1	9.8	6.8	5.1	9.0	3.0
III	..	22.5	15.9	15.6	16.8	16.7	12.3	8.4	6.0	4.7	3.5	1.3
IV	..	19.0	14.7	14.0	15.3	15.8	12.2	8.3	5.8	4.3	3.6	2.0
V	22.8	15.8	12.5	11.8	13.1	14.0	10.8	7.2	5.2	3.8	3.2	2.3
VI	11.8	9.0	6.9	8.0	9.7	11.0	9.4	5.6	2.8	1.9	1.1	
VII	9.8	8.3	6.2	7.1	8.7	10.0	8.7	5.3	3.9	3.0	2.3	2.0

Effects of Aging

It is apparent from Figure 1 that age, in general, increases the absorption in the ultraviolet. The curves are not proportional at all wave lengths, showing that the result is not due solely to the increase of one component. Instead, some curves touch at certain wave lengths and deviate widely at others. This behavior indicates that at least three absorbing components are present, the absorption maxima of which occur at differing wave lengths. This is especially evident in comparing aged rye and bourbon.

Although at present the nature of the compounds responsible for the absorption is not known, they are probably present in rather small amounts. The predominant absorption at 2760 Å. with minimum at 2500 Å. is somewhat similar to that of propionaldehyde (7). Furfural is rather different in its absorption but may be included. Acids probably account for much of the absorption at the lower wave lengths. The curves fall mostly in the order of age:

SAMPLE I is a 100-proof rye whisky 5 years old. It has the greatest absorption and the curve has several characteristic points. Comparison of the analysis (Table I) with that of the other whiskies does not show what causes the high absorption since only the volatile acids are in excess over the 5-year-old bourbon (II), and the 6-year-old mixed bourbon and rye (III). It would be interesting to determine the cause of this high absorption. It can hardly be ascribed entirely to volatile acids since these are reported to absorb ultraviolet light at the higher wave lengths and would not account for the high values at 2800 Å. Besides, sample III has a higher content of volatile acids than II; yet its absorption is less except for values under 2600 Å. Between 2350 and 2600 Å. the absorption is about the same for samples II and III.

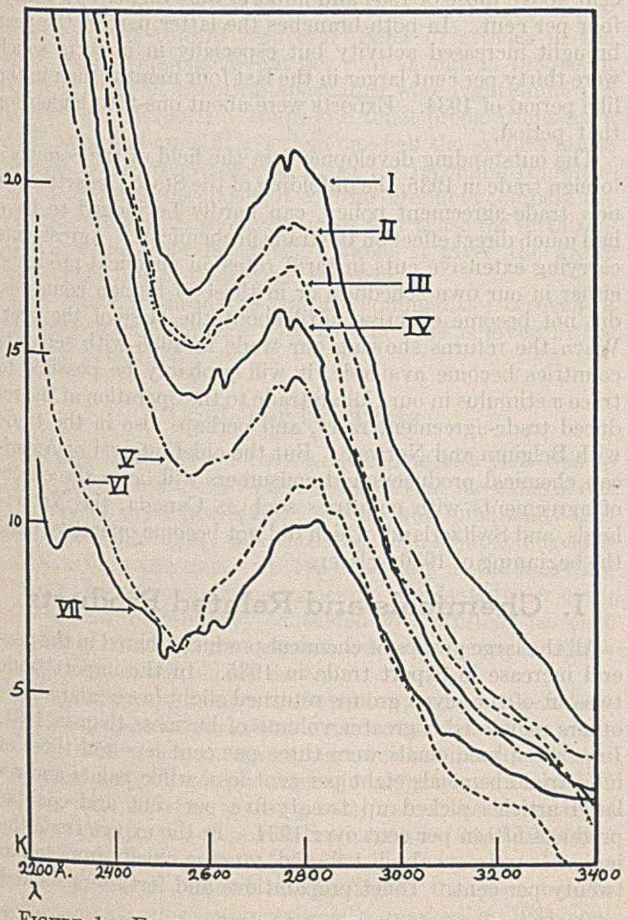

FIGURE 1. EFFECT OF AGE ON ULTRAVIOLET ABSORPTION OF WHISKIES

SAMPLE II is a 5-year-old 100-proof bourbon. The residue is higher than in sample I, as are the fixed acids, esters, and higher alcohols.

SAMPLE III is a 6-year-old mixture of bourbon and rye. The residue is low, the fixed acids are high, and the other values are intermediate between samples I and II. Since it is only 90 proof, the reactions that lead to increased absorption are evidently slower as the dilution alone is insufficient to account for the lower absorption.

SAMPLE IV consists of a mixture of 15 per cent 4-year-old with 6-month-old straight whisky. The residue, volatile acids, esters, and aldehydes all run considerably below the completely aged whiskies.

SAMPLE V is a straight 6-month-old whisky. The low residue and aldehyde values are of interest.

SAMPLE VI is a popular blend containing 20 per cent of 4-year-old whisky with alcohol. The high residue is accounted for by the presence of wine and caramel. Especially noticeable is the low absorption at 2500 Å. of blends VI and VII; this behavior gives an excellent method of recognizing a blended whisky; also that the peaks of curves VI and VII are displaced to the right of those of the straight whiskies.

SAMPLE VII is a blend containing 25 per cent of 6-month-old whisky with alcohol and caramel.

This summary of the analytical data shows that a chemical analysis fails to indicate why samples I, II, and III give such different absorption curves. We are thus led to the conclusion that the ultraviolet absorption spectra are due to the presence of substances that the ordinary chemical analysis fails to identify. If these substances contribute largely to the quality of the product, the use of ultraviolet spectrum analysis constitutes a new and significant method for the investi-

TABLE III. RELATIVE ABSORPTION OF SAMPLES LISTED IN DESCENDING ORDER

Wave length:	2400 Å.		2500 Å.		2600 Å.		2700 Å.		2800 Å.		2900 Å.		3000 Å.		3100 Å.			3200 Å.			3300 Å.			3400 Å.	
Dilution:	1-25	1-50	1-25	1-50	1-25	1-50	1-25	1-50	1-25	1-50	1-25	1-50	1-25	1-50	1-10	1-25	1-50	1-10	1-25	1-50	1-10	1-25	1-50	1-10	1-25
	I	I	I	I	I	I, II	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
	III	III	II	II	II	II, I	II	II	II	III	II	II	II	II	III	II	III	III	II	III	II	II	III	V	II
	II	II	III	III	III	III	III	III	III	II	III	III	III	III	II	III	II	II	III	V	III	III	V	II	V
	IV	...	IV	...	IV	...	IV	...	IV	...	IV	...	IV	...	IV	IV	...	V	IV	II	V	IV	II	III	IV
	V	V	V	V	V	V	V	V	V	V	V	V	V	V	V	V	V	IV	V	...	IV	V	...	IV	VII
	VI	...	VI	...	VI	...	VI	...	VI	...	VI	...	VI	...	VI	VII	...	VI	VII	...	VII	VII	...	VI	III
	VII	...	VII	...	VII	...	VII	...	VII	...	VII	...	VII	...	VII	VI	...	VII	VI	...	VI	VI	...	VII	VI

gation of the chemical changes that occur during the aging of whisky.

Acknowledgment

The author's thanks are due F. F. Heyroth for his help and counsel in this work.

This work on the ultraviolet absorption spectra of whiskies, though temporarily interrupted by lack of funds, will be continued.

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Chemical Foreign Trade in 1935

Continue[1] Trends Upward

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DESPITE a greater state of political tension abroad than at any other time since the World War, the year 1935 witnessed a continuation of the upward tendencies that have marked our foreign trade in chemical goods since 1932. The gain in imports was small but that in exports was of good proportions, thus repeating the story of the trade in 1934. In that year the gain in the incoming trade in chemical commodities was slightly under ten per cent and in the outgoing trade more than twenty per cent. In 1935 imports gained about five per cent over the previous year and exports eleven per cent. The spread between the two branches of the trade, which a few years ago were about the same in total value, has brought them to the point where imports are just two-thirds of exports in value.

Considering the 1923–25 trade as a fair average, our exports of chemical goods are now within sight of a normal level. Another year such as the last and they will have reached practically the value of the annual exports in that period. Imports, however, are still but little more than half the 1923–25 average and are making very slow headway toward that mark. As compared with the high figures of 1929, both imports and exports are still making a very deliberate recovery, the 1935 total for the former being forty-eight per cent of that in the boom year and for the latter sixty-eight per cent.

As compared with the total foreign trade of the United States in 1935 the combined incoming and outgoing movement of chemical goods showed a somewhat lower acceleration. Exports of all commodities taken together were seven per cent above those of 1934 and imports were higher by twenty-four per cent. In both branches the latter part of the year brought increased activity but especially in imports which were thirty per cent larger in the last four months than in the like period of 1934. Exports were about one-fifth higher for that period.

The outstanding development in the field of the country's foreign trade in 1935, the unfolding of the State Department's new trade-agreement policy, can hardly be judged to have had much direct effect on the trade in chemicals. Agreements carrying extensive cuts in tariff rates on chemical products, either in our own schedules or in those of foreign countries, did not become effective until about the close of the year. When the returns showing our trade in 1935 with separate countries become available, it will probably be possible to trace a stimulus in our Cuban trade to the operation of the reduced trade-agreement rates, and perhaps also in the trade with Belgium and Norway. But the chief interest of American chemical producers and consumers will lie in the effects of agreements with countries such as Canada, the Netherlands, and Switzerland, which did not become operative until the beginning of 1936 or later.

I. Chemicals and Related Products

All the large groups of chemical products shared in the general increase in export trade in 1935. In the import trade two out of the seven groups returned slight losses and all the others registered a greater volume of business than in 1934. Imports of medicinals were three per cent less and those of industrial chemicals eight per cent less, while paints and related articles picked up twenty-five per cent and coal-tar products fifteen per cent over 1934. In the export trade the increases were evenly distributed, ranging chiefly from ten to twenty per cent. Toilet preparations and fertilizers showed

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[1] All 1935 figures are preliminary. Import figures represent imports for consumption.

Table I. U. S. Foreign Trade in Chemicals by Total Values (in Thousands of Dollars)

Period	Imports	Exports	Period	Imports	Exports
1923–25 (av.)	$120,191	$116,267	1932	$47,958	$ 70,408
1929	143,106	152,109	1933	59,287	76,771
1930	112,048	127,855	1934	65,117	92,565
1931	82,780	100,094	1935	68,715	103,134

Table II. U. S. Foreign Trade in Chemicals by Great Groups (in Thousands of Dollars)

Imports	1929	1934	1935	Percentage Increase or Decrease, 1934–35
Coal-tar products	$22,321	$11,847	$13,558	+15
Medicinals and pharmaceuticals	6,194	4,237	4,128	− 3
Industrial chemicals	30,492	17,479	16,145	− 8
Pigments, paints, and varnishes	3,790	1,695	2,109	+25
Fertilizers and materials	72,351	26,029	28,561	+10
Explosives	1,020	593	827	+39
Soaps and toilet preparations	6,938	3,238	3,388	+ 4
Exports				
Coal-tar products	18,061	13,264	13,599	+ 3
Medicinals and pharmaceuticals	21,283	10,945	12,239	+12
Industrial chemical specialties	14,457	11,604	12,868	+11
Industrial chemicals	28,149	21,677	23,627	+ 9
Pigments, paints, and varnishes	29,111	14,207	16,345	+15
Fertilizers and materials	20,441	12,537	14,809	+18
Explosives, fuses, etc.	4,549	2,152	2,439	+13
Soaps	16,061	2,296	2,584	+13
Toilet preparations		3,884	4,624	+19

the largest gains but both were less than twenty per cent. The conservative increases in exports contrast rather strongly with the gains made in the previous year when fertilizers, for example, were sold to a value more than fifty per cent greater than in the year before.

As compared with the boom year 1929, exports of industrial chemicals and of chemical specialties have made the best record of progress toward recovery. Sales of articles in the former group were eighty-four per cent as high in 1935 as in 1929 and those of chemical specialties were eighty-nine per cent as high. Exports of soaps and toilet preparations have lagged most and are still less than one-half the exports in the last year before the depression. In the incoming trade the 1935 totals for medicinals and coal-tar products compare the most favorably with the 1929 totals and those for fertilizers and soaps the least favorably. Table II gives the group totals for the last two years and for 1929.

Last year's trade in the leading commodities of each of these groups as compared with that of 1934 is given in the following paragraphs.

Coal-Tar Products

The gain in exports of coal-tar products last year was so small and that in imports so considerable that the value of our purchases of these goods from abroad now practically balances that of our sales. The trade has been approaching such a balance for some time. In 1934 the gain in the incoming trade was heavy, amounting to nearly twenty-four per cent, and last year the tendency continued with a fifteen per cent increase; at the same time exports were registering increases of only seven and three per cent.

The speeding up of imports of coal-tar products was in evidence along the whole front, as considerable gains were registered in crudes, intermediates, and finished products alike. Dead or creosote oil was purchased in larger quantities and at higher prices, and the resulting total value was larger by a fourth than in 1934. The 1935 imports were 34,513,000 gallons with a value of $3,537,000, which compared with 31,774,000 gallons valued at $2,835,000 the year before. Price increases which were especially marked in 1934 continued through 1935, though at a reduced rate; the average valuation of these imports in 1935 was about ten cents as compared with nine cents in 1934 and six cents in 1933. The total value of this trade has more than tripled in two years. Imports of acids and other intermediates reached 2,052,000 pounds with a value of $2,448,000, also giving evidence of higher prices, for the 1934 shipments were 1,964,000 pounds valued at $1,976,000. After a slight recession in 1934 the trade in finished coal-tar products made a good recovery, reaching a total value of $6,349,000 as compared with $5,688,000 in 1934. Colors, dyes, and stains, as usual, made up the bulk of the imports, a total of 4,606,000 pounds valued at $6,034,000 being registered. Coal-tar medicinals were valued at $83,000, twelve per cent more than in 1934.

The export trade in coal-tar products was marked by a sharp falling off in shipments of crude coal tar and coal-tar pitch, a continuation of a decline extending back through 1934. In 1934 our exports of crude coal tar had a value of $1,149,000 whereas last year our sales of crude and refined together brought returns of only $364,000. Coal-tar pitch likewise fell from a 1934 value of $2,025,000 to only $895,000 last year. These figures represent a falling off of two-thirds to three-fourths in the last two years. These losses, however, were more than balanced by the handsome increases in other articles of this group. Colors, dyes, stains, and color lakes were sold abroad to the extent of 19,631,000 pounds with a value of $6,873,000, whereas in 1934 they were 17,942,000 pounds with a value of $5,630,000. Benzene shipments totaled 14,666,000 gallons and were valued at $2,513,000 as against 9,692,000 gallons valued at $1,761,000 in 1934, and creosote oil reached 349,000 gallons valued at $74,000 against a valuation of $42,000 the year before.

Medicinals and Pharmaceuticals

The falling-off in total value of imports under this heading last year was due to decreases registered by all three of the leading commodities in the group. Menthol imports were only 282,000 pounds with a value of $654,000, whereas in 1934 they totaled 425,000 pounds with a value of $848,000. Quinine sulfate dropped from 1,611,000 ounces valued at $688,000 to 1,442,000 valued at $646,000, and preparations in capsules, pills, tablets, etc., from a value of $622,000 to $589,000.

Each of the three principal classes of exports of medicinal and pharmaceutical preparations enjoyed greater sales last year. Biologics increased from $1,724,000 to $1,794,000, druggists' nonproprietary preparations from $3,404,000 to $3,862,000, and proprietary medicines from $5,528,000 to $6,248,000. In addition to these groups, white mineral oil was exported to the extent of 676,000 gallons valued at $285,000 as compared with 446,000 valued at $215,000, and castor oil to the extent of 40,000 gallons valued at $50,000 as against 54,000 valued at $66,000 in 1934.

Of the whole medicinal group the most important single item of export is that given as "tablets, pills, capsules, powders, and similar manufactures" for druggists. American goods of this type were sold abroad to the extent of $2,317,000 last year, a small increase over the 1934 figure of $2,122,000. Other druggists' preparations classified as "elixirs, cordials, tinctures, extracts, and similar liquid solutions" had a sale of $1,221,000 as compared with a round $1,000,000 the year before. A group of products classed as "tonics, blood purifiers, emulsions, and appetizers" consistently holds the lead in popularity among the foreign buyers of American proprietary medicines. In 1935 these goods reached an export value of $1,362,000 as against $1,159,000 in 1934. Salves and ointments sold abroad were valued at $1,044,000 in 1935 and $1,002,000 in 1934. The leading item among the biologics was serums and antitoxins for human use, exports of which were valued at $706,000 as against $669,000 in 1934.

TABLE III. IMPORTS AND EXPORTS OF INDUSTRIAL CHEMICALS (IN THOUSANDS)

	1934		1935	
Imports	Pounds	Value	Pounds	Value
Acetylene, butylene, ethylene, and propylene derivatives	607	$129	1,171	$254
Acids and anhydrides:				
Acetic or pyroligneous	29,817	1853	35,096	2079
Arsenious (white arsenic)	28,220	708	30,150	737
Formic	137	8	362	27
Oxalic	73	4	78	4
Sulfuric (oil of vitriol)	1,849	13	2,100	15
Tartaric	81	18	15	3
All other	1,928	446	1,829	434
Alcohols, including fusel oil	...	8	...	26
Ammonium compounds, n. e. s.:[a]				
Chloride (muriate)	6,159	154	7,855	187
Nitrate	5,111	76	3,517	54
All other	503	51	623	68
Barium compounds	1,703	69	1,881	61
Calcium compounds	708	17	483	10
Cellulose products, n. e. s.:[a]				
Acetate	6	9	7	43
All other:				
Sheets more than 0.003 inch thick, and other forms	111	99	135	126
Sheets and strips, more than 1 inch wide, not over 0.003 inch thick	32	17	271	53
Cobalt oxide	329	258	557	503
Copper sulfate (blue vitriol), gross weight	...	..	46	1
Glycerol, crude	15,081	1040	8,221	657
Glycerol, refined	2,214	209	69	8
Iodine, crude	1,481	2135	376	421
Lime, chlorinated, or bleaching powder	1,635	57	2,772	76
Magnesium compounds	9,729	151	7,686	121
Potassium compounds, n. e. s.:[a]				
Carbonate	13,006	802	4,125	232
Chlorate and perchlorate	10,801	594	14,317	752
Cyanide	81	33	99	39
Hydroxide (caustic)	4,016	259	3,427	226
Argols, tartar, and wine lees	13,979	885	16,368	903
All other	3,313	202	2,756	195
Sodium compounds, n. e. s.:[a]				
Sulfate (salt cake), tons	80	799	99	959
Sulfate, anhydrous, tons	8	151	5	114
Chlorate	1,909	82	2,533	162
Cyanide	20,530	2016	26,540	2930
Ferrocyanide (yellow prussiate)	1,121	95	663	52
Nitrite	2	[b]	10	1
Phosphate (except pyrophosphate)	13	2	3	[c]
All other	...	252	...	401
Radium salts grains (not in thousands)	339	1082	176	526
Other industrial chemicals	...	2687	...	2688
Exports				
Acids and anhydrides:				
Organic (exclusive of coal-tar acids)	1,798	243	3,147	290
Inorganic:				
Hydrochloric (muriatic)	4,041	65	6,558	98
Boric (boracic)	8,303	345	8,761	377
Other	9,651	420	9,878	352
Alcohols:				
Methyl, gallons	772	361	619	300
Butyl	3,358	332	2,135	205
Glycerol	[d]	[d]	3,354	450
Other	4,181	402	2,643	252
Acetone	3,534	324	2,884	296
Carbon disulfide	4,341	209	4,398	200
Formaldehyde (formalin)	2,598	125	2,498	134
Citrate of lime	6,181	371	1,579	109
Other organic chemicals	16,738	2574	21,236	3310
Nitro- or acetocellulose solutions, collodion, etc.	3,096	619	3,408	671
Aluminum sulfate	61,763	594	66,182	685
Other aluminum compounds	976	93	1,382	126
Calcium carbide	2,909	115	4,496	164
Calcium chloride	61,429	566	61,471	525
Copper sulfate (blue vitriol)	3,859	129	4,508	142
Hydrogen peroxide (or dioxide)	544	86	460	68
Potassium compounds, not fertilizers	4,242	467	7,281	637
Sodium compounds:				
Dichromate and chromate	8,350	493	7,301	464
Cyanide	611	89	1,006	141
Borate (borax)	207,287	2907	228,895	3242
Silicate (water glass)	21,304	213	15,758	203
Soda ash	66,863	962	87,050	1113
Sal soda	2,149	27	2,286	26
Bicarbonate (acid soda or baking soda)	15,196	254	13,477	227
Hydroxide (caustic soda) in drums	131,651	2992	139,138	2999
Sodium phosphate (mono-, di-, or tri-)	10,181	250	7,111	197
Other sodium compounds	19,529	785	20,840	863
Tin compounds	203	69	129	45
Gases, compressed, liquefied, and solidified:				
Ammonia, anhydrous	1,257	160	1,623	207
Chlorine	11,429	265	11,605	295
Other gases, n. e. s.[a]	22,357	512	23,070	674
Other industrial chemicals	...	3265	...	3538

[a] Not elsewhere specified.
[b] Less than 500 pounds.
[c] Less than $500.
[d] Not separately stated.

Industrial Chemical Specialties

This group is made up of a varied list of preparations for household and farm use which have become widely popular in the many countries to which, as American specialties, they have penetrated. They are listed only among the exports.

The leading item in the group from year to year is "household and industrial insecticides and exterminators," which in liquid form sold abroad last year to a value of $1,093,000, and in powdered or paste forms, $110,000. In 1934 sales were $976,000 and $145,000, respectively. Agricultural insecticides, fungicides, etc., enjoy a steadily growing sale, the trade in 1935 reaching $1,066,000 as against $935,000 the year before. Nicotine sulfate, calcium arsenate, and lead arsenate are in greatest demand. Rubber-compounding agents, valued at $774,000, were one of the few items to show a loss, the 1934 total having been $830,000. Cementing preparations rose from $611,000 to $660,000, petroleum jelly from $776,000 to $799,000, and leather dressings and stains from $324,000 to $385,000, while dextrin or British gum fell from a 1934 figure of $605,000 to $225,000 in 1935 and baking powder from $572,000 to $469,000.

Industrial Chemicals

The spread between our purchases and our sales of articles in this class was still further increased in 1935 when imports failed to reach the total of the year before while exports continued to mark up their usual gain. Our sales of these goods last year were about fifty per cent more than our purchases. Details of the trade are shown in Table III.

Pigments, Paints, and Varnishes

Both the incoming and the outgoing trade in this class of goods showed a healthy increase in 1935. The trade is largely exporting, the value of shipments abroad being usually about eight times as great as that of receipts of foreign goods.

There was a large increase in our purchases of the principal commodity among the imports last year, iron oxide and hydroxide. Shipments totaled 19,889,000 pounds and were valued at $442,000, about fifty per cent more in both quantity and value than in 1934. Ochers and siennas also recorded a large increase, shipments amounting to 12,631,000 pounds, valued at $254,000, as against the previous year's total of 9,185,000 pounds valued at $180,000. The trade in lithopone and zinc pigments, which had dropped sharply in 1934, recovered part of the ground lost; the 1935 totals were 9,206,000 pounds and $257,000, and those for 1934 were 7,854,000 pounds and $220,000. Zinc oxide and leaded zinc oxide, 3,982,000 pounds valued at $205,000, also picked up from a 1934 slump which sent the trade down to 2,534,000 pounds valued at $149,000. Paints, stains, and enamels, however, failed to follow the example of the raw materials, imports attaining a value of only $287,000 as against $330,000 in 1934 and $489,000 in 1933, and varnishes registering only $20,000 as against $24,000 in 1934 and $32,000 in 1933.

After dropping off about one-fifth in volume in 1934, our exports of carbon black or gas black showed a healthy recovery last year which brought them back most of the ground they had lost. Shipments totaled 142,185,000 pounds as compared with 120,620,000 in 1934 and 152,286,000 in 1933. Prices held up well, and the total value of the trade reached $6,673,000. In 1934 it was $5,541,000, about the same as in 1933.

The large gain in exports of ready-mixed paints, stains, and enamels recorded in 1934 was capped by a still further gain, smaller in extent but still considerable, in 1935. Sales totaled 2,175,000 gallons and were valued at $3,805,000, those of the previous year being 1,813,000 gallons valued at $3,271,000.

Pyroxylin lacquers continue to enjoy an increased demand abroad. Exports of pigmented lacquers, standing at 426,000 gallons and valued at $1,008,000, were practically the same as in 1934 but clear lacquers increased from 87,000 to 101,000 gallons and from a valuation of $179,000 to $211,000, and thinners from 500,000 gallons valued at $423,000 to 651,000 gallons valued at $519,000.

Among the other larger items in the export trade in this group the following were the most important: Varnishes (oil or spirit and liquid driers), $520,000, a fourteen per cent gain; bituminous paints, liquid and plastic, $411,000, practically the same as in 1934; calcimine or cold-water paints, dry, $313,000, a gain of twenty-six per cent; paste paints, $302,000, a gain of twenty per cent. The chief item among the mineral earth exports (ocher, umber, sienna, and other forms of iron oxide) reached a value of $278,000, slightly more than in 1934. The leading chemical pigment aside from carbon black is lithopone, sales of which were valued at $222,000, or about eleven per cent more than in 1934. Zinc oxide, $171,000, showed a thirteen per cent loss. White lead, $278,000, and red lead, $99,000, registered gains of thirty-seven and three per cent, respectively.

Fertilizers

The two outstanding features of last year's foreign trade in fertilizers and materials were the continued rapid decline in imports of ammonium sulfate and the continued rise in imports of sodium nitrate. Ammonium sulfate imports were only 79,000 tons with a value of $1,760,000, whereas in 1934 they were 185,000 tons valued at $3,656,000. This is a decrease of nearly 60 per cent. The 1934 trade, however, was itself far below that of the preceding year and the present falling off is simply a part of the two-year decline. In 1933 we imported 351,000 tons of ammonium sulfate valued at $6,179,000. In two years, therefore, this trade decreased seventy-five to eighty per cent.

Sodium nitrate imports, on the other hand (123,000 tons valued at $2,343,000 in 1933), rose to 294,000 tons in 1934 and to 391,000 tons in 1935, the value showing a corresponding increase to $5,672,000 in 1934 and $7,940,000 in 1935. Thus in two years the trade gained nearly two hundred and twenty per cent in volume and two hundred and forty per cent in value. Checking these changes against each other we find that in two years the drop in value of ammonium sulfate imports amounting to $4,419,000 was more than matched by the gain of $5,597,000 in imports of sodium nitrate. The average valuation of the sodium nitrate imports has shown a tendency to increase slightly, that for 1935 standing at about $20.30 per ton as compared with $19.30 in 1934 and $19.05 in 1933.

Calcium cyanamide imports stood at 100,000 tons valued at $2,359,000 in 1935, a considerable gain over the previous year's figure of 82,000 tons valued at $1,893,000. Calcium nitrate imports, 23,000 tons valued at $593,000, compared with 1934 imports of a value of $598,000; urea and calurea, $410,000, compared with $462,000 in 1934; guano, $312,000, compared with $337,000, and dried blood, $386,000, with $151,000 in 1934. Ammonium nitrate mixtures (not containing phosphoric acid or potash) were one of the leading import items in 1935, totaling 32,000 tons valued at $753,000.

Imports of phosphate fertilizers were valued at $752,000 in 1935 as compared with $556,000 in 1934. Potash imports were mostly much higher, as shown in Table IV.

Exports of land-pebble phosphate rock showed a considerable gain in 1935, amounting to 975,000 tons as compared with 896,000 in 1934. The value of the trade rose correspondingly from $4,336,000 to $4,956,000. High-grade hard rock also made notable gains, the 1935 shipments of 130,000 tons valued at $818,000 comparing with shipments with a total value of $673,000 in 1934. Superphosphate exports fell to a value of $534,000 from the 1934 total of $606,000. In the nitrogenous group ammonium sulfate exports reached 78,000 tons valued at $2,040,000. In 1934 the value of this trade was only $714,000. Other nitrogenous chemical materials were valued at $3,134,000 and nitrogenous organic waste materials at $198,000. The total value of nitrogenous-fertilizer exports stood at $5,371,000 last year as against $4,935,000 in 1934. Potassic fertilizer materials ($1,992,000) were more than twice the 1934 figure ($918,000), but exports of chemical fertilizers classed as nitrogenous-phosphatic types were valued at $797,000 as compared with $751,000 in 1934.

TABLE IV. IMPORTS OF POTASH FERTILIZERS (IN THOUSANDS)

	1934		1935	
	Tons	Value	Tons	Value
Chloride, crude	127	$3672	234	$4,744
Kainite	115	1116	74	590
Manure salts	78	1029	85	1,054
Sulfate	62	1950	86	2,530
Nitrate (saltpeter)	32	1071	40	1,244
Total	414	8838	519	10,162

Explosives

Firecrackers were the only item of importance in this group imported in 1935. They totaled 3,797,000 pounds and were valued at $792,000. Their 1934 value was $548,000. Dynamite, the leading export, was shipped abroad to a value of $1,261,000 in 1935 as against $916,000 in 1934. Safety fuses reached a value of $537,000 as compared with $459,000 in 1934 and blasting caps $385,000 as compared with $314,000.

Soaps and Toilet Preparations

A small decrease in the most important import item under this heading, perfume materials, which fell in value from $1,591,000 to $1,478,000, and a drop in imports of perfumery, bay rum, and toilet water from $680,000 in 1934 to $562,000 in 1935, were more than offset by considerable increases in the imports of soap, which rose from $759,000 to $1,162,000 in 1935. Castile soap reached a value of $232,000 as against $212,000 in 1934.

Dental creams, as usual, were the leading item of export. The 1935 trade was valued at $1,409,000, a considerable gain over the $1,219,000 of the year before. These exports increased 40 per cent in the last two years. Sales of toilet or fancy soap increased from $856,000 in 1934 to $1,073,000 in 1935; hair preparations from $356,000 to $388,000; manicuring preparations from $232,000 to $274,000; talcum powder in packages from $390,000 to $458,000; and scouring soap, bricks, pastes, and powders from $228,000 to $252,000. Laundry soap sold to a value of $636,000 last year as against $640,000 the year before.

II. Materials Related to Chemical Industries

The groups of commodities already mentioned include the chief chemicals and chemical products entering into our foreign trade. A number of others related more or less closely to chemical industry have a place in our commerce with other countries and may be discussed here.

Mineral Oils

Both imports and exports of petroleum and petroleum products continue to gain in total value. Details of the trade in the last two years are shown in Table V.

TABLE V. FOREIGN TRADE IN PETROLEUM AND PRODUCTS (IN THOUSANDS)

Imports	1934 Barrels	1934 Value	1935 Barrels	1935 Value
Petroleum and products, total	...	$36,521	...	$37,346
Petroleum, crude	35,772	25,903	32,513	23,517
Advanced and refined oils	14,870	9,532	22,201	13,293
Exports				
Petroleum and products, total	...	227,537	...	249,104
Petroleum, crude	41,127	49,756	51,430	61,176
Natural gasoline	1,495	2,729	1,645	3,335
Refined oils:				
Gasoline, naphtha, and other finished light products	21,565	51,233	26,721	63,716
Illuminating oil (kerosene)	9,607	20,792	6,455	15,184
Gas oil and distillate fuel oil	13,398	17,883	14,351	17,484
Residual fuel oil	12,579	10,459	11,334	9,533
Lubricating oil	7,511	58,234	8,305	61,571
Fuel or bunker oil for vessels in foreign trade (not included in exports)	29,899	31,264	30,304	29,925

Sulfur

A decrease in crude sulfur exports and an increase in shipments of refined sulfur marked the 1935 trade in this commodity. Exports of crude dropped from 507,000 tons valued at $9,365,000 in 1934 to 402,000 valued at $7,582,000 in 1935. Refined, crushed, ground, and sublimed sulfur, and sulfur flowers were sent abroad to the extent of 24,452,000 pounds valued at $419,000. In 1934 the trade amounted to 22,652,000 pounds valued at $398,000.

Vegetable and Essential Oils

Olive oil was imported in notably larger quantities in 1935, the total trade amounting to 70,789,000 pounds with a value of $8,758,000 as compared with 56,000,000 pounds valued at $6,989,000 the year before. Imports of sunflower-seed oil were valued at $2,220,000, five times the 1934 importations, and those of corn oil at $1,571,000, more than three times the 1934 value. Other edible vegetable oils imported in large amounts included cottonseed oil, 166,687,000 pounds valued at $8,880,000; palm-kernel oil, 7,978,000 pounds valued at $294,000; and peanut oil, 80,723,000 pounds valued at $3,367,000.

TABLE VI. IMPORTS OF ESSENTIAL OILS (IN THOUSANDS)

	1934 Pounds	1934 Value	1935 Pounds	1935 Value
Cassia and cinnamon	378	$243	451	$347
Geranium	146	693	123	563
Attar of roses, ounces	26	206	36	273
Bergamot	78	106	99	135
Citronella and lemon grass	2186	724	2048	579
Lavender	298	704	226	509
Lemon	193	136	131	131
Orange	140	155	161	171
Sandalwood	[a]	[a]	3	11
Lime	47	240	64	299
All other	..	1283	..	1396
Total		4490		4414

[a] Sandalwood oil imports, 141 pounds valued at $1442.

In the face of the processing tax, coconut oil was shipped to this country from the Philippines in greatly increased amounts in 1935, and the value was especially large compared with that of recent years. A total of 353,396,000 pounds of coconut oil came from those islands as compared with 314,802,000 pounds in 1934 and 316,078,000 pounds in 1933. The value was $12,576,000 last year, $7,372,000 in 1934, and $8,556,000 in 1933. Imports of tung oil were even greater in value than those of coconut oil, totaling $13,131,000, as compared with only $6,852,000 in 1934 and $4,833,000 in 1933. The great increase in total value was due chiefly to higher prices as the volume of shipments, 120,059,000 pounds, was only about nine per cent over the 1934 figure of 110,007,000 pounds, and was little larger than that of 1933, 118,760,000 pounds.

Palm oil imports were third in importance with 296,502,000 pounds valued at $8,542,000, the 1934 trade being 155,531,000 pounds valued at $3,905,000. Perilla oil increased in value from $1,613,000 in 1934 to $4,384,000 in 1935, carnauba wax from $1,528,000 to $2,789,000, and sulfured olive oil from $1,958,000 to $2,058,000.

The trade in essential oils varied considerably from the 1934 figures, recording both increases and decreases. Table VI shows the totals for the last two years.

In the export trade, shipments of the two leading essential oils were considerably increased over 1934. Peppermint oil exports were valued at $865,000 and pine oil at $582,000, comparing, respectively, with $679,000 and $502,000 in 1934. Citrus oils advanced to a place of much importance in the trade, exports amounting to 337,000 pounds and being valued at $283,000.

Dyeing and Tanning Materials

Imports of dyeing and tanning materials were somewhat heavier in 1935 than in the year before, being valued at $6,184,000 as against $5,777,000. Quebracho extract accounted for half the total with imports of 110,439,000 pounds valued at $3,172,000 as against 125,086,000 valued at $2,870,000 in 1934. Quebracho wood was the second most valuable import, but it dropped in value from $747,000 in 1934 to $409,000 last year. Valonia ($319,000) and gambier ($303,000) were the only other articles to reach a value of $300,000 in 1935. Exports of dyeing and tanning extracts were valued at $1,967,000 in 1935 and $1,924,000 in 1934. Last year's total was made up chiefly of vegetable and chemical tanning extracts valued at $1,617,000, besides chestnut extract exports of $172,000.

Rubber

The quantity, the value, and the price of our rubber imports all showed increases in 1935. A total of 1,045,380,000 pounds was imported as against 1,036,268,000 in 1934. The total value was $119,082,000 as against $101,573,000, and the unit value 11.4 as against 9.8 cents. Balata imports continued to decline, being valued at $188,000 in 1935 and $438,000 in 1934. Two years ago they reached $2,262,000.

Gums, Resins, and Naval Stores

Unbleached shellac continued to lead all other imports of gums and resins in value in 1935, imports of 19,726,000 pounds being valued at $2,669,000. In the previous year they were valued at $1,686,000. Bleached shellac fell from a value of $125,000 in 1934 to $68,000 in 1935, and seed lac, crude lac, etc., from $1,127,000 to $853,000. Chicle imports reached a total of 7,775,000 pounds valued at $1,887,000 as compared with 1934 shipments of 6,499,000 pounds valued at $1,471,000. Crude natural camphor dropped from $646,000 in 1934 to $422,000 last year, and refined natural from $570,000 to $499,000; synthetic camphor rose from $258,000 to $321,000.

Exports of naval stores, gums, and resins were as shown in Table VII for the last two years.

TABLE VII. EXPORTS OF NAVAL STORES, GUMS, AND RESINS (IN THOUSANDS)

	1934 Quantity	1934 Value	1935 Quantity	1935 Value
Naval stores:				
Gum rosin, barrels	794	$6,615	918	$7,794
Wood rosin, barrels	231	1,778	276	2,200
Gum spirits of turpentine, gallons	9789	4,755	10,380	4,895
Wood turpentine, gallons	893	403	945	430
Tar and pitch of wood, barrels	9	98	10	97
Other gums and resins, pounds	5090	840	6,193	1,073
Total		14,489		16,489

RECEIVED February 6, 1936.

LIQUID DIELECTRICS

Effect of Soluble Oxidation Products on Power Factor and Conductivity of Liquid Paraffin

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Power factor and conductivity measurements have been made on liquid paraffin containing various concentrations of nine compounds selected to represent the common types of oxidation products that are formed by the oxidation of hydrocarbons. While in homogeneous solution in the oil, none of these compounds in reasonable concentrations caused sufficiently large increases in the power factor and the conductivity of the oil to be considered of practical significance in high-voltage cables. Upon separating from solution as a soft gel, however, one of the compounds produced a power factor many times greater than that of the oil.

AS HAS been pointed out in recent reviews on the behavior of liquid dielectrics (*5*, *11*), very little is known concerning the nature of the charge carriers that give rise to dielectric losses in insulating oils. The contributing effect upon the losses produced by the several types of substances which may be present in commercial oils as constituents or as impurities, or which may be formed by conditions of service, are likewise largely unknown. Except for water (*9*, *10*) and rosin (*6*) the available data seem to be concerned with the total effect upon the power factor and the conductivity of oil or oil-and-paper insulation caused by given treatments, such as oxidation, rather than with the effect produced by the various specific types of products which may be formed by these treatments. For instance, it is known that, when an insulating oil is oxidized, its power factor and conductivity generally increase. At the same time, it is known that, by the oxidation of a hydrocarbon, a variety of products may be formed such as moisture, acids, aldehydes, alcohols, and more or less chemically inert polymerization or condensation products. The concentrations of some of these products have been determined analytically and comparisons attempted between the analytical results and the dielectric behavior of the oils (*7*, *12*). Since other products besides the type or types analytically determined may be formed by the oxidation of hydrocarbons, however, it is not known whether the changes in dielectric behavior are due primarily to the formation of any one or more of the chemical types of oxidation products present, such as acids, or to the combined effect of such products with the moisture formed, or to the oil-insoluble bodies formed in the course of the oxidation, or to still other causes. Since information of this type, concerning not only oxidation reactions but also reactions produced by corona discharge, seems necessary in order to explain some of the data obtained by this company during the past several years, an investigation of the effect of the presence of various oil-soluble chemical structures and oil-insoluble bodies on the power factor and the conductivity of insulating oils has been undertaken. One of the primary objects of the work is to differentiate between the types of materials which contribute seriously to dielectric losses at 60 cycles and those which do not.

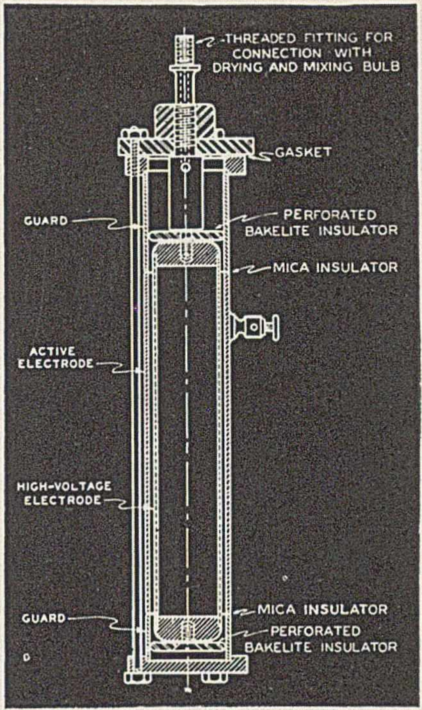

FIGURE 1. CELL FOR POWER FACTOR AND CONDUCTIVITY MEASUREMENTS

The present paper deals with one phase of this problem—namely, the effect of some oil-soluble oxidation products upon the power factor and the conductivity of solutions of these products in liquid paraffin. The mode of approach to the problem consisted simply in adding to the liquid paraffin a known amount of the substance being investigated and determining the power factor and the conductivity of the resulting solution.

Apparatus

The cell used for the power factor and conductivity measurements is shown in longitudinal section in Figure 1:

This cell is made of stainless steel and consists of two concentric cylinders, the inner cylinder serving as the high-voltage elec-

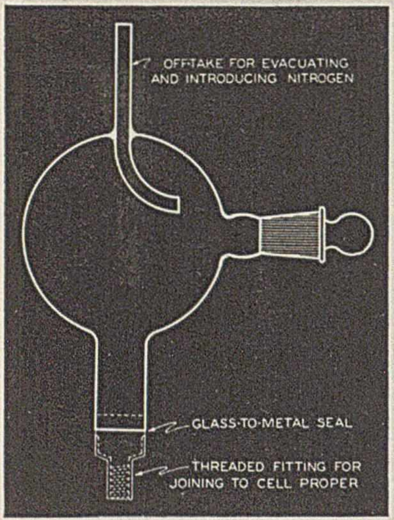

Figure 2. Bulb for Drying and Mixing Test Samples

trode and the outer cylinder, in three closely held units, serving as the active electrode and guards. Mica is used to insulate the active electrode from the guards. The high-voltage electrode is centered by means of two perforated Bakelite insulators; the electrode spacing is 1.8 mm. (0.071 inch). A 30-ml. sample is required to fill the cell.

A 200-ml. glass bulb (Figure 2) fitted with a ground-glass stopper and an offtake for evacuating and introducing nitrogen is screwed to the top of the cell by means of a glass-to-metal seal, the metal part of which is gold-plated. This bulb is used in drying the sample of oil to be tested and in mixing the various oxidation products with the sample.

The power factor measurements were made with a modified Schering bridge (*8*) at a voltage stress of 1970 volts per mm. (50 volts per mil), and at a frequency of 60 cycles. For making the d. c. conductivity measurements, a Leeds & Northrup insulation testing set No. 5600 was used. These measurements were made at a voltage stress of 98.5 volts per mm. (2.5 volts per mil).

Materials and Procedure

The base oil, to which the various substances were added, was a water-white liquid paraffin having a viscosity of 285 Saybolt Universal seconds at 40° C. and 50.5 Saybolt Universal seconds at 100° C. This oil was chosen in preference to commercial cable oil because different samples had been found to have a low and nearly uniform power factor, and because the oil contained only small traces of oxidation products and colloidal materials. [This oil, Stanolind Liquid Paraffin, Heavy, was obtained from the Standard Oil Company (Indiana). According to the Technical Department of that company the "Stanolind Liquid Paraffin has been thoroughly refined with strong reagents so as to meet United States Pharmacopeia specifications. As a result, this product is a saturated hydrocarbon oil. . . . . . ."] Some of the physical properties of the oil as furnished by the manufacturer are:

Specific gravity at 15.6° C.	0.8860
Flash point, ° C.	201
Pour point, ° C.	−17.8

The compounds added to the oil were selected to represent the simple chemical types of products which are formed by the oxidation of insulating oils and which are soluble in those oils. In order not to interfere with the technic employed, very volatile compounds were avoided. The compounds selected, together with brief notes concerning their solubility behavior and the methods by which they were dried and purified, are listed in Table I. All the chemicals were of the best quality obtainable from the Eastman Kodak Company and were colorless with the exception of the naphthenic acids in which a straw color persisted even after repeated distillations.

Power factor and conductivity measurements were made on each sample of base oil alone and again after the compound was added, the following procedure being employed:

Table I. Compounds Used to Represent Chemical Types Formed by Oxidation of Hydrocarbons

Chemical Type	Compound Used	Method of: Drying[a]	Method of: Purification	Solubility Behavior
Acid	Stearic acid	*a*	*c*	*f*
	Mixed naphthenic acids (neutralizing equivalent, 180)	*b*	*c, d*	*g*
	Propionic acid	*b*	*c*	*g*
Aldehyde	Valeraldehyde	*b*	*c*	*g*
	Heptaldehyde	*b*	*c*	*g*
Ketone	Methyl *n*-amyl ketone	*b*	*c*	*g*
Alcohol	Cetyl alcohol	*a*	*c*	*f*
Ester	Cetyl acetate	*b*	*c*	*g*
Peroxide	Benzoyl peroxide	*a*	*e*	*f*

[a] Symbols are as follows:
a. Dried by heating below boiling point under partial vacuum.
b. Dried in contact with anhydrous calcium sulfate.
c. Freshly distilled in all glass apparatus under reduced pressure.
d. Redistilled twice, the last time in a Hickman still (*4*).
e. Dissolved in c. p. benzene centrifuged to remove a trace of insoluble impurity.
f. Higher concentrations separated upon cooling.
g. Soluble at all temperatures and concentrations used.

A 30-ml. sample of the base oil was dried and degassed in the mixing bulb at 80° C. for half an hour under a pressure of approximately 1 mm. of mercury. The power factor cell and mixing bulb were then placed in an upright position, and dry nitrogen was admitted to the mixing bulb to force the oil into the power factor cell and to raise the pressure to atmospheric. Power factor and conductivity measurements were then made at selected temperatures. The average results of these measurements on the base oil are shown in Figure 3. The results of any given test varied only slightly from the indicated averages.

In order to introduce the compound into the oil, the power factor cell and mixing bulb were placed in an inverted position, and the bulb was evacuated to draw the oil out of the power factor cell; then dry nitrogen was admitted to restore the pressure to atmospheric. A weighed amount of compound was introduced through the glass-stoppered opening in the side of the mixing bulb, and the bulb was agitated and if necessary warmed to effect solution of the compound in the oil. The solution was returned to the power factor cell by reëvacuating the system, placing the cell in an upright position, and again admitting dry nitrogen. Power factor and conductivity measurements were then made on the solution at selected temperatures.

Because of the reported instability of the benzoyl peroxide (*1*, *2*, *3*), this material was at no time heated above 65° C. The solutions of benzoyl peroxide were made by adding to the oil a benzene solution of the peroxide and removing the benzene under reduced pressure at 60° C.

The concentrations of the compounds used were selected to cover more than the range of the total concentration of oxidation products encountered in service-aged mineral insulating oils, especially high-voltage underground cable oils, unless they had been subjected to unusually drastic treatment.

Discussion of Results

The power factor data for the solutions of each of the compounds in liquid paraffin are shown graphically in Figure 4, and the corresponding conductivity data for several of them in Figure 5.

As has been stated, one of the primary objects of this work was to obtain evidence to determine whether the presence of certain oxidation products in homogeneous solution in insulating oils produces sufficient increases in power factor and conductivity to be of practical significance. As will be seen from the data, regardless of chemical structure or difference in molecular weight,

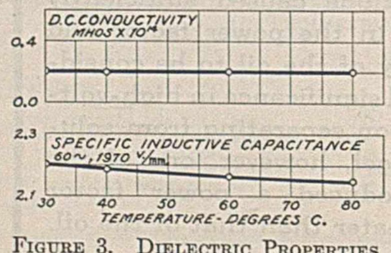

Figure 3. Dielectric Properties of Base Oil

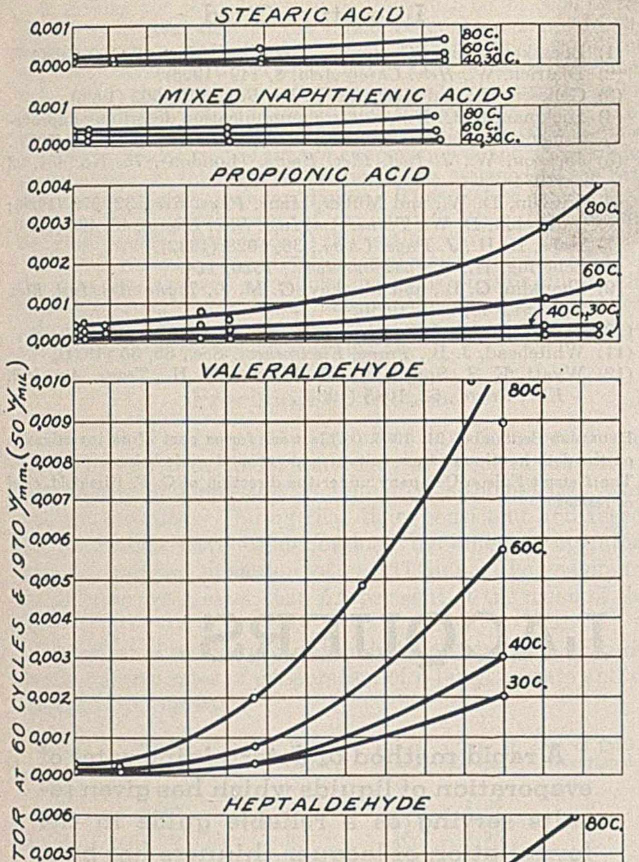

FIGURE 4. EFFECT OF SOLUBLE OXIDATION PRODUCTS ON POWER FACTOR OF LIQUID PARAFFIN

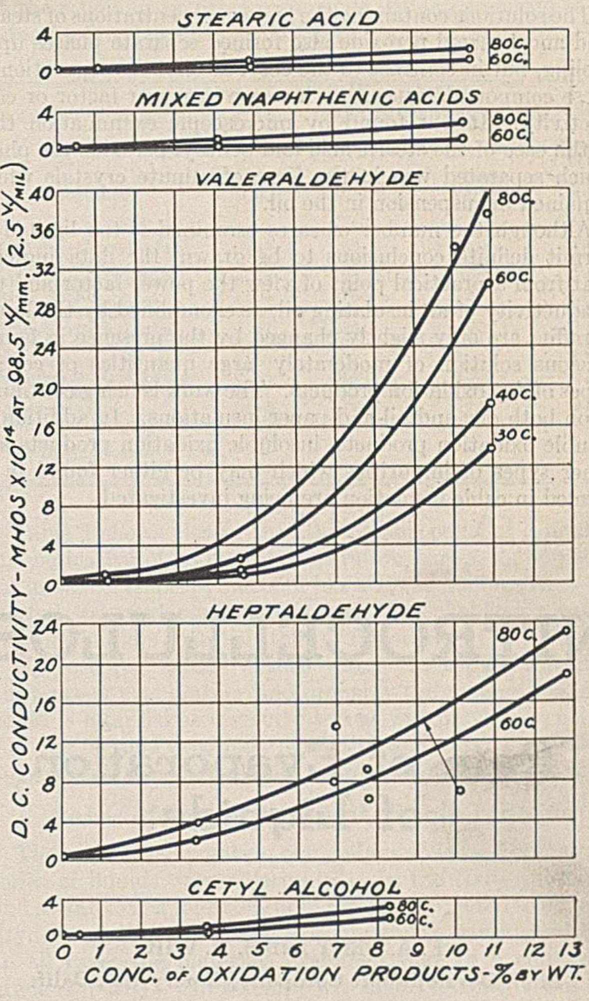

FIGURE 5. EFFECT OF SOLUBLE OXIDATION PRODUCTS ON CONDUCTIVITY OF LIQUID PARAFFIN

none of the compounds tested caused significant changes in the power factor and the conductivity of the liquid paraffin, even at 80° C., so long as the concentrations were not over 5 per cent. Changes of a magnitude approaching practical significance were produced only by the two aldehydes, and then only when in concentrations of 8 to 10 per cent. Such concentrations of aldehydes are much higher than are found even in badly oxidized oils. It is entirely possible, moreover, that a part of the power factor and the conductivity increases for the aldehydes may have been due to partial decomposition or polymerization of the aldehydes. Although diligent effort was made to prepare uniformly pure samples, difficulty was experienced in obtaining reproducible results. Some of the values obtained were higher and some lower than the values shown by the curves. One of such values for the heptaldehyde is indicated by an arrow on Figures 4 and 5. No such difficulty was experienced in working with the other compounds. A further difference between the aldehyde solutions and the other solutions was that the power factor and the conductivity of the aldehyde solutions increased considerably with time, whereas the other solutions were quite stable.

While none of the compounds had much effect upon the power factor and the conductivity of the liquid paraffin so long as the compounds were in homogeneous solution in the oil, one of the compounds had a marked effect upon separating from the oil. As has been indicated in Table I, although all the substances were selected with the view of producing homogeneous solutions, the higher concentrations of three of them formed separate phases upon cooling. In the case of the highest concentration of cetyl alcohol measured, the power factor at 30° C. increased from 0.0001 to over 0.1 during a few minutes. The conductivity also increased but not in proportion to the power factor increase. Investigation revealed that part of the cetyl alcohol was no longer in solution but had separated as a soft gel or as an emulsion.

The solutions containing the higher concentrations of stearic acid and benzoyl peroxide also formed separate phases upon cooling, but in contrast to the cetyl alcohol the separation of these compounds caused no increase in power factor or conductivity. It was found by microscopic examination that in the case of the stearic acid and benzoyl peroxide the phase which separated was in the form of minute crystals which remained in suspension in the oil.

Although the number of cases examined is too limited to permit definite conclusions to be drawn, the data indicate that from a practical point of view the power factor and the conductivity of an insulating oil, as exemplified by the liquid paraffin, are only slightly changed by the presence in homogeneous solution of moderately large quantities of certain types of dry oxidation products. The work is being continued upon both oils and oil-and-paper insulations. In addition to soluble oxidation products, insoluble oxidation products and other types of impurities which may be either found in or formed in cable insulation are being investigated.

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RECEIVED September 21, 1935. This work forms part of an investigation on the deterioration of high-voltage underground cable being conducted by The Detroit Edison Company under the direction of C. F. Hirshfeld, chief of research.

NITROCELLULOSE LACQUERS

Rate of Evaporation of Liquids

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A rapid method of determining rates of evaporation of liquids which has given results serving as a reliable guide in the formulation of lacquer thinners has been developed. A comparison of this method with others prevailing in the lacquer industry is made. The rates of evaporation were determined for various classes of organic solvents and diluents used in the lacquer solvents and diluents used in the lacquer industry. The rates of evaporation of the liquid components of a lacquer influence the structure and appearance of the final film.

⑤ IN FORMULATING thinners and lacquers, data are needed on the relative rates of evaporation of the various solvents and diluents in order to determine whether, in the practical applications of these solvents and diluents, their initial solubility relations for nitrocellulose and resins may be disturbed during the drying. If a proper balance of solubility is not maintained throughout the drying of the lacquer, the solid ingredients may be precipitated with a consequent loss of the desirable qualities of the resulting film.

In spite of the importance of a knowledge of the rate of evaporation of solvents and thinners, no standard method of determining this property of liquids has been adopted by the lacquer industry. In an important article Hofmann (*3*) correlates the results of various methods of determining rates of evaporation with the results he obtained using a modification of a method described by Polcich and Fritz (*4*). This modified method cannot, however, be used in the rapid determination of rates of evaporation of several liquids at the same time; hence a single determination cannot give comparative data on the rate of a number of liquids. A method similar to that of the writers for measuring the relative rates of evaporation of liquids is mentioned in an article (*1*) which appeared while the present report was being prepared. Almost certainly the results obtainable with the two methods will check closely.

Data on single liquids or mixtures of liquids are taken with the apparatus described in the following pages. The absolute rates of evaporation of solvents and diluents usually change somewhat when these materials are added to lacquer mixtures, but the relative rates, which are measured with this apparatus, are preserved during the evaporation unless the materials form constant-evaporating mixtures.

Method and Apparatus

The time required for the complete evaporation of a definite amount of each liquid exposed to a draught of air is the important measurement in the empirical method developed for comparing the rates of evaporation of liquids:

An electric fan, mounted on a turntable which revolves at a speed of 4 revolutions per minute, extends through a hole in the center of a platform. The blades of the fan, inclined at an angle of 70° to the horizontal, send an intermittent current of air over and into a set of aluminum pans which contain the evaporating liquids. The aluminum pans, 2 inches (5 cm.) in diameter, 0.5 inch (1.27 cm.) in depth, and containing a close-fitting filter paper, are fixed in position on the platform in a circle around the fan. The filter paper insures uniform wetting and hence a uniform evaporating surface during the final stages of the evaporation, when the various liquids may otherwise expose greatly different evaporation areas. Figure 1 is a view of the platform from above showing the pans arranged about the fan: Figure 2 shows, from beneath the platform, the mechanism driving the turntable.

In making the test, duplicate portions of 5 cc. of each of the liquids under test and of the liquid taken as a standard are measured with a pipet into the aluminum pans which are placed in position on the platform while the fan and turntable are in motion. The time from the initial exposure to the current of air to the time for complete evaporation of the liquids is noted. The time of evaporation of the standard liquid (usually *n*-butyl acetate) is divided by the time of evaporation of the liquid under examination; in this way the value 1.00 is assigned to the rate of evaporation of the standard liquid. Thus, values greater than 1.00 indicate greater rates of evaporation than that of the standard liquid; those under 1.00, smaller rates.

When it is desired to obtain an evaporation curve of a liquid, the pans are removed at regular intervals of time during the evaporation, tightly covered, and weighed on an analytical balance. The curve is constructed by plotting loss of weight against time on rectangular coördinates.

Precision of Method

The method and apparatus described have been used during the last three years under different conditions of laboratory temperature and probably of humidity, although the latter was not recorded. During that time, consistent and reproducible results have been obtained by different operators with an average deviation of ±0.11 unit; the maximum deviation is not greater than 5.6 per cent of the mean of the rates.

The effect of ordinary variation in laboratory temperatures on the relative rates of evaporation of *n*-butyl acetate and of toluene is as follows:

Room Temp.	Rate of Evapn.[a]	No. of Detns. Averaged	Room Temp.	Rate of Evapn.[a]	No. of Detns. Averaged
° C.			° C.		
19	1.96	2	24	1.95	9
20	1.94	2	25	1.95	5
21	1.92	6	26	1.95	1
22	1.95	8	27	1.93	2
23	1.95	8			

[a] Ratio of *n*-butyl acetate to toluene.

It is apparent that the average variation of temperature throughout the year in this laboratory has little effect on the relative rates of evaporation of toluene and *n*-butyl acetate.

Evaporation Process

When liquids are evaporated using this method, equilibrium between the liquid and vapor phases is never attained, because the molecules are swept away from the surface of the liquid by the draught of air. In this way, evaporation of the liquid is greatly accelerated. The necessary heat required for vaporization is supplied from the surrounding air and the platform, with the result that evaporation always goes on at temperatures below that of the room. The thermal and molecular properties which control evaporation during this process are not discussed, for they have not been investigated separately; but such inherent properties, although affecting an absolute measurement of the rate of evaporation, necessarily all affect a relative measurement of the rate of evaporation of a liquid. However, it may be of interest to consider the effect of probable association of molecules as indicated by the latent heat of vaporization (measured at the boiling point) by comparing this property with the relative rates of evaporation and the boiling points of several aliphatic alcohols and ethers.

The relative rates of evaporation of alcohols and ethers arranged in the order of their boiling points are shown in Table I, referred to the rate of *n*-butyl acetate as unity.

TABLE I. COMPARISON OF VOLATILITY OF ETHERS AND ALCOHOLS

Substance	Rate of Evapn.[a]	B. P. at 760 Mm.	Mol. Weight	Latent Heat of Vaporization
		° C.		Cal./g.
Methyl *tert*-butyl ether	7.40	55.2	88	76.8
Methyl alcohol	3.70	64.7	32	262.2
Ethyl *tert*-butyl ether	6.40	72.8	102	74.3
Ethyl alcohol	2.05	78.3	46	202.2
Isopropyl alcohol	2.08	82.4	60	161.1
Methyl *tert*-amyl ether	4.57	86.3	102	72.8
sec-Butyl alcohol	0.96	99.5	74	134.4
Ethyl *tert*-amyl ether	3.43	101	116	73.1
sec-Butyl *tert*-butyl ether	2.25	114	130	...
sec-Amyl alcohol	0.47	115–119	88	...
n-Butyl alcohol	0.44	117	74	141.2
n-Butyl *tert*-butyl ether	1.26	123	130	...

[a] *n*-Butyl acetate = 1.00.

Table I shows clearly that the boiling point of a liquid is not indicative of its rate of evaporation, except for homologs; for instance, isopropyl alcohol has a lower boiling point than methyl *tert*-amyl ether, yet isopropyl alcohol has a rate of evaporation less than half that of the ether.

Hygroscopic liquids absorb water from the atmosphere during their evaporation, and probably the evaporation of the liquid is retarded as a result; but as was previously pointed out, the method described is relative and affords a measurement which does not require correction for practical usage.

Rates of Evaporation of Single Liquids

The rates of evaporation of members of several homologous series of liquids were determined. In the tests, the liquids and a sample of a reference liquid were evaporated to complete dryness at the same time and under the same conditions. In all cases the materials examined were of a commercial grade of purity. No attempt was made to control the temperature of the room, the humidity of the atmosphere, or the temperature in the evaporating liquid.

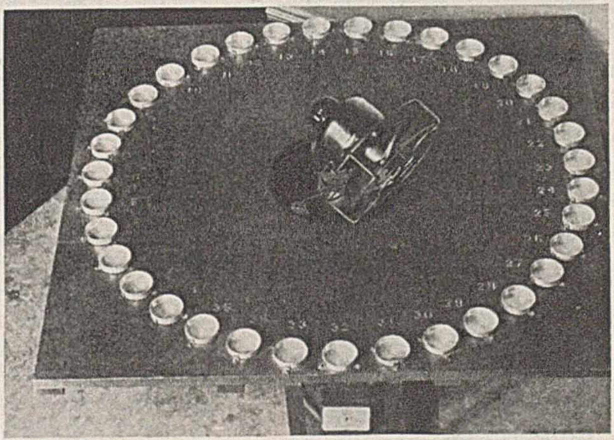


FIGURE 1. TOP VIEW OF PLATFORM

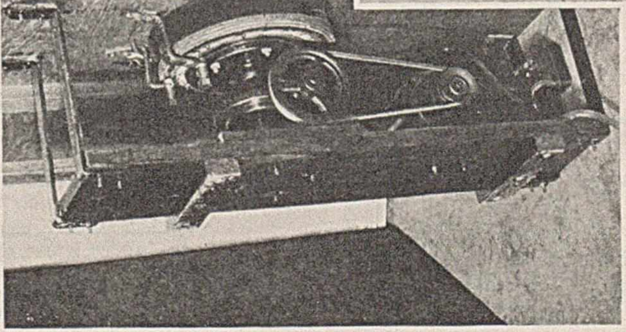


FIGURE 2. DRIVING MECHANISM OF FAN TURNTABLE

TABLE II. RATE OF EVAPORATION OF VARIOUS LIQUIDS

Substance	Rate of Evaporation[a]	Boiling Point ° C.	Mol. Weight
Acetic Esters of Lower Aliphatic Alcohols			
Methyl acetate	7.15	57	74
Ethyl acetate	4.95	77	88
Isopropyl acetate	3.13	92	102
sec-Butyl acetate	1.78	112	116
n-Butyl acetate	1.00	126.5	116
sec-Amyl acetate	0.83	131–133.5	130
Pentacetate	0.56	126–155	130
sec-Hexyl acetate	0.34	146–156	144
Ketones			
Acetone	7.70	56	58
Methyl ethyl ketone	4.59	79.6	72
Methyl propyl ketone	2.02	102	86
Methyl butyl ketone	0.60	127	90
Cyclohexanone	0.24	155	98
Lower Alcohols			
Methyl	3.70	64.7	32
Abs. ethyl	2.65	78.3	46.1
95% No. 3A C. D. ethyl	1.86	78.1	...
Isopropyl	2.08	82.4	60.1
n-Butyl	0.44	117	74.1
Isobutyl	1.48	107	74.1
sec-Butyl	0.96	99.5	74.1
tert-Butyl	1.92	82.3	74.1
sec-Amyl	0.47	116–119	88.1
tert-Amyl	0.85	101.8	88.1
Ethers			
Methyl *tert*-butyl	7.40	55	88
Methyl *tert*-amyl	4.57	86.3	102
Ethyl *tert*-butyl	6.40	72.8	102
Ethyl *tert*-amyl	3.43	101	116
n-Butyl *tert*-butyl	1.26	123	130
sec-Butyl *tert*-butyl	2.25	114	130
Aromatic Hydrocarbons			
Benzene	4.76	80.2	78.1
Toluene	1.96	110.7	92.1
Xylene	0.55	131.5	106.1
Ethylbenzene	0.89	135.8	106.1

[a] Ratio of time of evaporation of *n*-butyl acetate to that of the liquid.

TABLE III. RATES OF EVAPORATION OF ALIPHATIC HYDROCARBON DILUENTS

Substance	Manufacturer or Supplier	Rate of Evaporation[a]	
		Toluene = 1.00	*n*-BuAc = 1.0
Lacquer Diluent A	Shell Oil Co.	2.85	5.38
Lacquer Diluent B	Shell Oil Co.	0.32	0.60
Lacquer Diluent C	Shell Oil Co.	1.20	2.26
TS-11	Shell Oil Co.	0.44	0.89
Rotosolve	Shell Oil Co.	0.30	0.57
P. & V. Thinner	Shell Oil Co.	0.22	0.11
Benzo-Sol	Shell Petroleum Corp.	4.40	8.65
Tolu-Sol	Shell Petroleum Corp.	1.83	3.58
Diisobutylene	Shell Development Co.	1.68	3.29
Union Oil Solvent No. 8	Union Oil Co. of Calif.	1.17	2.36
"10" Toluene Substitute	Union Oil Co. of Calif.	1.22	2.30
B. & L. Thinner	Standard Oil Co. of Calif.	2.17	4.25
Troluoil	Anderson Pritchard Co.	1.44	2.88
Cook Co.'s. naphtha	Cook Paint & Varnish Co.	1.11	2.20
Petroleum ether	W. P. Fuller & Co.	0.79	1.55

[a] Time of evaporation of standard to that of the liquid.

TABLE IV. COMPARISON OF FAN METHOD WITH MODIFIED POLCICH AND FRITZ METHOD USED BY HOFMANN

Substance	Rate of Evaporation		
	Polcich-Fritz method	Bent-Wik method (× 100)	Calcn. of Rate of Evapn.[a]
Ethyl acetate	485	495	582
sec-Butyl acetate	162	178	180
sec-Amyl acetate	73	83	85
n-Butyl acetate	100	100	100
95% ethyl alcohol	193	186	186
sec-Butyl alcohol	110	96	87.5
n-Butyl alcohol	45.7	44	31.7
Acetone	850	770	975
Toluene	186	194	186
Xylene	65.5	55	62

[a] (Vapor pressure × mol. weight)/11.

The rates of evaporation of various liquids are given in Table II.

Aliphatic hydrocarbons derived from petroleum have been used extensively by the lacquer industry as substitutes for toluene. The rates of evaporation of some petroleum diluents commercially available are shown in Table III.

De Heen (2) found that the quantity of a liquid evaporated in a given time interval is proportional to the product of the vapor pressure and the molecular weight. Hofmann confirmed de Heen's findings and showed that approximately accurate results can be calculated from the formula:

$$(\text{Vapor pressure} \times \text{mol. weight})/11 = \text{rate of evaporation}$$

The proportionality factor depends upon the conditions under which the evaporation takes place. This formula, with the constant $^1/_{11}$, shows the approximate relative rate of evaporation of a liquid at 25° C., referred to *n*-butyl acetate.

The rates of several liquids measured by Hofmann are compared in Table IV to rates of evaporation calculated by de Heen's formula and also to rates of evaporation measured by the writers.

A good agreement is found between the values for the rates of evaporation measured by the modified Polcich-Fritz method and measured by the method developed here. Both methods afford results in fair agreement with the calculated values.

Time-evaporation curves of several petroleum aliphatic hydrocarbon diluents obtained from the Shell Petroleum Corporation are shown in Figure 3, compared to time-evaporation curves of toluene and *n*-butyl acetate. This method of representation has the value of depicting all stages of evaporation of a liquid. Such curves can also be used to express relative rates at any stage of evaporation by dividing the time required for a certain volume of a reference liquid to evaporate, by the time required to evaporate an equal volume of the liquid under test. Similarly, an instantaneous relative rate of evaporation can be found from the slopes of the curves of the liquid under test and the reference liquid.

Rates of Evaporation of Binary Mixtures

When a blend of two liquids which do not form a constant-evaporating mixture is evaporated to complete dryness, the time of evaporation is almost linear with the initial composition. That is, when the times of evaporation to complete dryness of a number of mixtures of the two liquids of different composition are plotted against the initial composition of the mixtures, the resulting curve is almost a straight line and can be so considered for practical purposes of formulation. Several such mixtures which apparently do not form constant-evaporating mixtures, are shown in Figures 4 and 5. The average relative rate of evaporation of a particular composition of any two of the components which are plotted can be obtained by dividing the time of evaporation of the reference liquid by the time of evaporation of the mixture.

When two liquids form a constant-evaporating mixture,

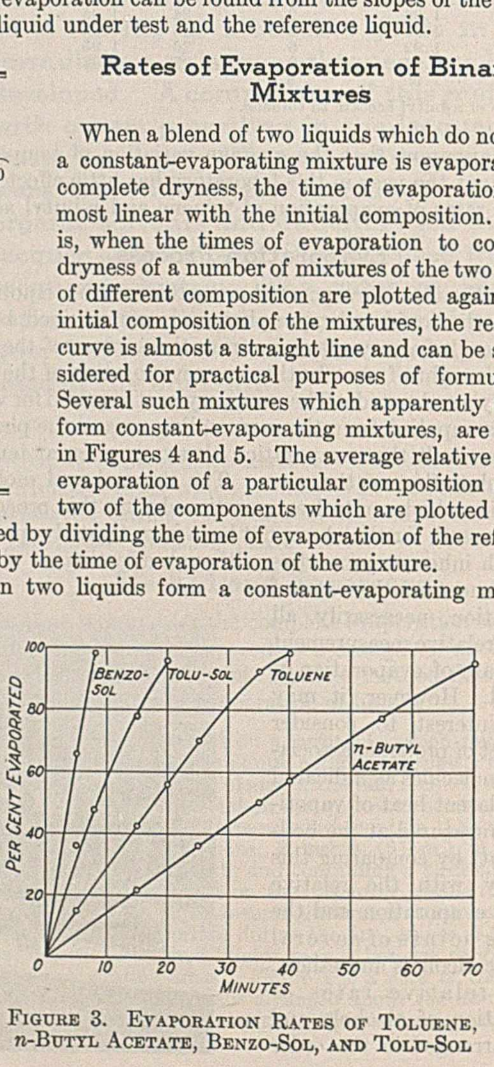
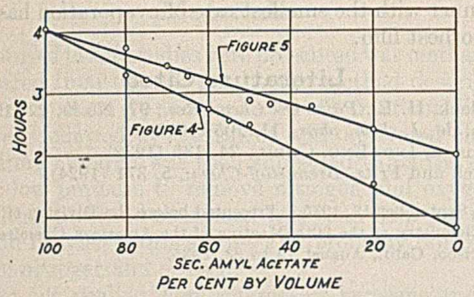


FIGURE 3. EVAPORATION RATES OF TOLUENE, *n*-BUTYL ACETATE, BENZO-SOL, AND TOLU-SOL



Figures 4 and 5. Evaporation Rates of Binary Mixtures (10-Cc. Samples)

Figure 4. Methyl ethyl ketone and *sec*-amyl acetate
Figure 5. *sec*-Butyl acetate and *sec*-amyl acetate

the curve showing initial composition of different mixtures plotted against their time of evaporation is not a straight line. Such a curve is shown in Figure 6, representing mixtures of methyl ethyl ketone and a petroleum hydrocarbon diluent. It is not known just which constituent of the diluent used is responsible for this singularity, but the case illustrated is unique, for methyl ethyl ketone does not form constant-evaporating mixtures with the ordinary petroleum hydrocarbon diluents. Constant-evaporating mixtures are, however, likely to be formed from the components of ordinary lacquers, and unless this is kept in mind, the rate of evaporation of the final mixture will not be that predicted from a consideration of the rates of evaporation of the individual components of the lacquer.

Selection of Evaporation Data

There is some difference of opinion as to the relative value of evaporation data expressed graphically by time-evaporation curves, or expressed as time to total dryness in terms of a standard reference liquid. Some lacquer chemists believe that the first 30 to 40 per cent evaporated is the fraction of the lacquer which introduces water into the film and causes roughness or "orange peel" and that the following 30 to 40 per cent is most effective in removing any water and roughness of the film which may be present. Another view is that data giving relative evaporation to total dryness are most important. Both methods of expressing evaporation data appear to be of use.

Graphical representation either by time-evaporation curves or by average relative evaporation curves is especially applicable to the comparison of mixtures to indicate the evenness of evaporation. The writers do not believe that a time-evaporation curve of the liquid portion of a lacquer can be used to predict whether or not a lacquer will give, on drying, a smooth or a rough film. It seems more probable that the ultimate quality of the film will depend on the viscosity of the nitrocellulose lacquer just prior to drying. A controlling factor of viscosity is the solvent power for nitrocellulose of the liquid in its final evaporation stages; accordingly, the method of expressing data by relative evaporation to total dryness appears to be of more practical value. From such data we can predict the relative time each component will remain in the lacquer during its drying period, and from this knowledge balance the solvent power of the mixture throughout the drying period by a proper combination of diluents (nonsolvents) and solvents for nitrocellulose. This view appears to be supported by the consideration expressed in the following paragraphs.

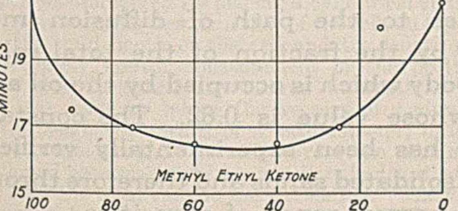


Figure 6. Curve Indicating that Binary Mixtures of Methyl Ethyl Ketone and Petroleum Hydrocarbon Diluent Form Constant-Evaporating Mixtures (5-Cc. Samples)

Effect of Rate of Evaporation of Lacquer Ingredients on Film Formation

The rates of evaporation of the liquid components of a lacquer determine, in part, the appearance of the film which is obtained by applying the lacquer to a surface. Evaporation of the liquid components begins immediately when the lacquer is applied to an exposed surface. If the lacquer is sprayed, a portion of the liquid components of the lacquer is evaporated during the transit from the spray gun to the surface. After the lacquer has covered the surface, evaporation continues and the lacquer is said to "flow out." A lacquer has good flow when the film settles to a perfectly smooth, even surface, with good gloss. If the liquid components leave the drying film too rapidly, the viscosity of the lacquer may increase rapidly, and a pitted uneven surface may result because the excrescences will not have had time to level out. In general, fast-evaporating lacquers show a coarse structure.

To illustrate this point, three different lacquers were made using the same base lacquer blended with thinners of different rates of evaporation. The initial excess tolerance was the same in each case, as were also the proportions of thinner to base lacquer. These lacquers were sprayed in a similar manner on to

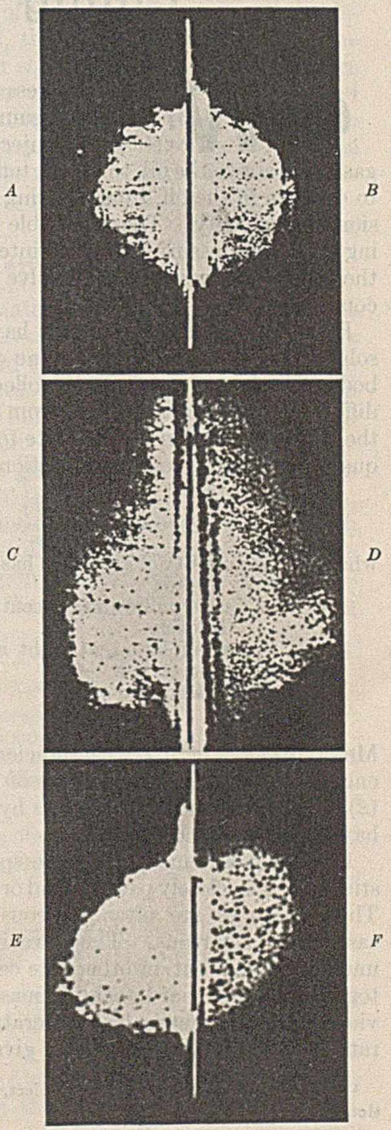


Figure 7. Effect of Evaporation Rate of Lacquer Thinner on Film Formation

A, C, E. Reference lacquers
B. Lacquer containing slow-evaporating thinner
D. Lacquer containing medium-evaporating thinner
F. Lacquer containing fast-evaporating thinner

glass plates, the sprayed portion was next covered, and then the adjoining section of each plate was sprayed with the same base lacquer blended with a slow-drying thinner. The photomicrographs of Figure 7 indicate not only the similarity of spraying technic, by comparing the films on the left of the dividing line in each photograph, but also the differences between the structures of films of fast-drying and slow-drying lacquers, by comparing the films on either side of the line. The rate of evaporation of the thinners used in these tests increases in the order of the numbers. It is clear that in this case thinner with the smallest rate of evaporation has yielded the smoothest film.

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RATES OF SOLUTION OF GASES IN OILS[1]

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Rate of Solution of Methane in Oils Filling Spaces between Sand Grains

When the pressure within a partially depleted petroleum formation has been increased by injection of natural gas to the gas dome above the oil, there is a tendency for some of the gas to dissolve in the oil, thus lowering its viscosity, surface tension, and density. These possible favorable changes resulting from "repressuring" create interest in the rate at which the gas may be expected to dissolve under different prevailing conditions.

Previous experiments (*2*, *3*, *6*) have shown that the rate of solution of a gas such as methane or propane in a quiescent body of hydrocarbon oil is controlled primarily by the rate of diffusion of the dissolved gas from the gas-oil interface into the body of the liquid. The rate for such a process is given quantitatively, up to half-saturation, by the equation:

$$Q = 2\,C_s A \sqrt{\frac{D\,t}{\pi}}$$

where Q = quantity of gas which has passed through surface
C_s = final equilibrium concentration of gas in solution
A = area of liquid, at right angles to direction of flow
D = diffusion constant
t = time

Methods of predicting, with sufficient accuracy for engineering purposes, the values of D for methane (*2*) and for propane (*3*) in various hydrocarbon oils have been proposed.

Petroleum is found in the pore spaces or interstices between closely packed sand or rock particles. These particles are often siliceous but in some cases are calcareous. They are in many cases unconsolidated but in others are cemented firmly together to form hard rocklike masses. It is obvious from geometrical considerations that the rate of solution of a gas in a given oil will be different when the oil is held within and completely fills the interstices of such a sand mass than when it is in the form of an oil body free of sand. The effective cross section will be less and the path of diffusion will be longer in carrying dissolved gas to the same depth below the gas-oil interface. It has been suggested (*1*) that the case of oil held in a sand may be complicated by surface effects due to the presence of large amounts of sand-oil interface which might assist the solution process.

It was the purpose of the present investigation to develop methods of utilizing the constants for gases dissolving in oils determined by previous experiments, for the more practical case of oils held in unconsolidated silica sands. It was also desired to ascertain whether the effect of the presence of sand was merely geometrical in character.

A study of the rate of solution of gaseous methane in hydrocarbon oils entirely filling the interstices of closely packed silica sands has shown that the process is substantially the same as for the case of quiescent oils in the absence of sand.

In the case with sands present, the over-all area at right angles to the path of diffusion must be multiplied by the fraction of the total volume of the sand body which is occupied by the oil and by a constant whose value is 0.82. The constancy of this factor has been experimentally verified only with unconsolidated sands and therefore throughout a relatively narrow range of porosities.

Electrical conductance experiments upon copper sulfate solutions held in similar sand bodies gave practically the same value of the constant, indicating that the effect of the sand is only geometrical.

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[1] For other articles on this general subject, see literature citations *2*, *3*, *6*.

Materials

The gas used in the studies here presented was methane. It was prepared from natural gas by the method described by Sage and co-workers (*7*) and consisted of a fractional liquefaction process followed by treatment with activated charcoal. The resulting material was then subjected to partial solidification at low pressure to remove nitrogen and oxygen (*2*). The resulting methane contained less than 0.02 per cent of ethane and heavier hydrocarbons and probably not over 0.1 per cent of nitrogen and oxygen.

The two oils studied were samples of kerosene and spray oil used by Hill and Lacey (*2*). They were chosen in order to connect the present measurements directly with the results of the earlier work. These two oils had markedly different properties as shown by the values obtained by the earlier authors and reproduced in Table I. The diffusion constant for methane in kerosene was found to be 3.4 times that for methane in spray oil.

The sand samples used were screened lots of naturally occurring silica sands. The 20–30 mesh sand (through a 20-mesh screen but retained upon a 30-mesh screen) was standard Ottawa sand. The other samples were cuts from sands mined in Nevada. All the samples had densities within 1 per cent of each other.

Table I. Properties of Oils

Oil sample:	Kerosene	Spray Oil
Sp. gr. (86° F./39.1° F.)	0.7944	0.8617
Gravity, °A. P. I. (60° F.)	44.2	30.7
Viscosity, centipoises	1.42	13.45
Av. mol. weight	167	287

Methods

Measurements of rates of solution were made with the same apparatus and by substantially the same methods as were reported by Hill and Lacey (*2*). The technic was complicated by the problem of obtaining a densely packed sand body whose interstices were completely filled with the oil samples and contained a minimum of trapped air bubbles. The best method of obtaining uniform and reproducible dense packing was as follows:

> Ten or fifteen milliliters of the oil were placed in the steel absorption-rate cell, and enough sand was added to take up almost all of the kerosene in its void spaces. The cell was then given a swirling motion to release trapped air bubbles. Next the cell was vigorously tapped on a heavy wooden block for several minutes. Another similar addition of oil and sand was made, and the process continued until all of the sample of sand had been added. A level upper surface was obtained by placing the cell in a special wooden vise, which held it level, and then tapping the bottom of the cell. The fraction of the total volume of the sand mass which corresponded to the void spaces between the grains was determined for each size range of sand in the following manner: A known weight of sand was packed into the cell with kerosene as described above, and the depth of the sand layer in the cell was measured by placing a cylindrical steel slug, whose diameter was slightly less than that of the cell, on top of the sand. Since the total depth of the cell and the length of the slug were accurately known, measurement of the protruding height of the slug furnished the desired information. This measurement was made by taking the average of a number of readings of the height by means of a cathetometer, observing from different points around the cell. From the diameter of the cell, which had been machined accurately cylindrical, and the height of the sand the total volume was calculated. The volume of the sand grains alone was ascertained from weight of sand and its density as determined by the pycnometer method. The volume of voids was given by difference. The values used were in each case the average of several different measurements, the maximum deviation from the mean being in all cases less than 0.8 per cent. All other methods of packing and measurement which were tried proved to be less reproducible than the one outlined.

In making solution rate determinations, 2 to 3 ml. more oil were used than was necessary to fill the void spaces of the sand. This precaution served to insure that the oil level did not drop below the top of the sand when subjected to the higher pressure of the methane gas. Any small bubbles of air entrapped during the packing process would shrink upon the increase of pressure to about 5 per cent of their earlier volume. More satisfactory experimental results were obtained when no wetted sand was exposed above the surface of the oil. The thin layer of oil above the sand level, together with the wetted interior surface of the bomb walls above the liquid level, produced more rapid solution rates during a few minutes at the start of a run but these films soon became practically saturated and thereafter the rate of solution depended only on the rate of diffusion of dissolved gas through oil in the sand mass. These rapid earlier rates in no way interfered with later measurements.

After the charge of sand and oil in the steel cell was prepared, the cell was closed and connected to the methane measuring and supply system. This system and the method of using it were the same, except for minor improvements, as were described by Hill and Lacey (*2*). In the runs with sand the air present above the oil was not evacuated from the cell because preliminary trials showed that this operation resulted in disturbing the sand packing to such an extent as to render results unreliable. It was therefore necessary to use the partial pressure of methane rather than the total pressure of gas in the cell for purposes of the calculations. In all the determinations here reported, the partial pressure of methane was close to 300 pounds per square inch and the temperature was 86.0° F. (30° C.). The experimental runs were carried far enough to establish definitely the slope of the straight line obtained by plotting the amount of gas dissolved against the square root of the time. The runs were carried in most cases to approximately 40 per cent of saturation of the oil.

Experimental Results

In order to be sure that materials and experimental technic were comparable to those used in the earlier work, runs were made using the kerosene and the spray oil without sand. In each case values of C_s and of D were obtained which agreed with the values reported by Hill and Lacey (*2*) for 86° F. well within the experimental error.

In the diffusion equation given, area A, in the case when no sand is present, is equal to the area of the cell cross section. When sand is present, the mean effective liquid area through which diffusion takes place will be dependent upon the cross-sectional area of the cell, upon the percentage of void spaces in the sand body, and upon the deviation of path around sand grains. In this case,

$$A' = A\ V\ B$$

where A = cross-sectional area of cell
V = fraction voids in sand mass
B = constant for conversion of mean horizontal liquid area to mean effective area for diffusion

Substituting this expression for A in the diffusion equation, putting in m (corrected slope) for $Q/\sqrt{t}$, and solving for B:

$$B = \frac{m\ \pi^{1/2}}{2\ A\ V\ C_s D^{1/2}}$$

The results of the rate determinations in the presence of sand are presented in Table II. Those for kerosene are arranged in order of decreasing grain size of the sand used. Values of uncorrected slope obtained directly from the straight line resulting from plotting the experimental values of the volume of methane admitted to the cell *vs.* the square root of the time were corrected for minor deviations of the methane partial pressure from 300 pounds per square inch and for the fact that the volume of the solution changed as the dissolving process proceeded. These corrections were made in the same manner and using the same values of ϵ as were given in previous papers (*2*, *6*). Using the above equation and keeping units consistent, values of B were calculated for all the runs on the assumption that the sand does not affect the values of C, and D, being only a geometrical agent.

TABLE II. RESULTS OF RATE OF SOLUTION MEASUREMENTS

Run No.	Mesh-Size Range of Sand	Fraction Voids, V	Effective Area Constant, B
	Methane in Kerosene		
36	20– 30	0.3097	0.835
37	20– 30	0.3097	0.837
39	30– 40	0.3231	0.834
40	30– 40	0.3231	0.833
41	40– 50	0.3325	0.821
42	40– 50	0.3325	0.826
33	50– 70	0.3455	0.813
35	50– 70	0.3455	0.817
32	100–140	0.3728	0.819
34	100–140	0.3728	0.820
38	100–140	0.3728	0.820
	Methane in Spray Oil		
44	20– 30	0.3097	0.863
45	20– 30	0.3097	0.844

The highest and lowest values of B for kerosene differ by 3 per cent which is within the experimental error of the measurements. The highest values are found in the cases of the coarsest sands where geometrical edge effects would be expected to have the greatest influence, increasing the effective area. For these reasons the value of B may be considered constant for the case of kerosene and independent of the grain size of the sand. A value of $B = 0.82$ is taken as the most probable one.

In the case of methane dissolving in spray oil, the mean value of B is 0.853 and is somewhat higher than the value for kerosene with the same sand, 0.836. However, when one considers that the value of the diffusion constant, D, for spray oil is less than one-third that for kerosene, while the corresponding values of B differ by only 2 per cent, it may be inferred tentatively that the value of 0.82 for B can be used for different oils, within engineering accuracy.

The empirical constant B might be purely geometrical or might be influenced by changes of diffusion rate due to gas adsorption at the sand-oil interfaces. This latter possibility seemed somewhat unlikely, especially since B remained substantially constant with two oils of markedly different diffusion rates. However, it was thought to be desirable to test this possibility by studying a process which involved the same geometrical factor due to the sand but in which the diffusion of dissolved gas and its possible adsorption were eliminated. Electrical conductance measurements have been used effectively to determine the necessary geometrical factors to be applied in complex heat conduction problems (*4*). The conductance method has also been applied to the case of salted gelatin suspensions of sand (*5*).

A series of electrical conductance studies was therefore made using the same samples of sands as before, packed in a similar manner. The measurements were made in a cell with glass side walls cemented into a plane copper base. Copper sulfate solution in water was the liquid used. The sand packing in this case could not be made quite as reproducible as in the steel cell, but was measured in each case. After the cell charge was packed and the fraction of void spaces was determined, an upper horizontal copper electrode, closely fitting inside the glass walls, was lowered until in contact with the upper sand surface. The distance from the upper surface of the copper base, which acted as the lower electrode, to the lower surface of the upper electrode was determined by a series of readings with the cathetometer. The electrical resistance of the cell was then measured by the methods usual in conductance studies. Similar resistance measurements were made with the same copper sulfate solution without sand in the cell to determine its specific conductance.

For the case with no sand present the specific conductance

$$K = L/A\,R$$

where L = distance between electrodes
A = cross-sectional area of cell
R = resistance of solution between electrodes in cell

However, when sand is present, both the effective area of the cell and the length of path between the electrodes will be altered. The mean effective area of the cell $A' = A\,V\,B$. The volume of solution in the sand mass $= A\,L\,V$ and since the effective area is $A\,V\,B$, the mean effective length of path $= A\,L\,V/A\,V\,B = L/B$. The specific conductance,

$$K = \frac{L/B}{A\,V\,B\,R} = \frac{L}{A\,V\,B^2\,R}$$

$$B = \sqrt{\frac{L}{K\,A\,V\,R}}$$

The results of the conductivity cell measurements are summarized in Table III. The same trend in values of B is seen, those for the coarse sands being slightly higher. Nevertheless, B remains constant within experimental error. Considering the difference in the processes and apparatus for the two sets of determinations, the values of B from them are surprisingly close together. The authors interpret this fact as indicating that the diffusion of dissolved gas through an oil held in the interstices of a silica sand mass is not appreciably affected by the presence of the sand particles except in a geometrical manner.

TABLE III. RESULTS OF CONDUCTANCE MEASUREMENTS

Run No.	Mesh-Size Range of Sand	Fraction Voids, V	Effective Area Constant, B	Run No.	Mesh-Size Range of Sand	Fraction Voids, V	Effective Area Constant, B
13	20–30	0.3178	0.803	27	40–50	0.3387	0.796
14	20–30	0.3182	0.800	17	50–70	0.3488	0.790
15	20–30	0.3193	0.798	18	50–70	0.3484	0.791
16	20–30	0.3239	0.804	19	50–70	0.3507	0.790
21	30–40	0.3280	0.794	20	50–70	0.3489	0.792
22	30–40	0.3337	0.795	24	100–140	0.3808	0.786
23	30–40	0.3315	0.797	25	100–140	0.3808	0.787
26	40–50	0.3436	0.798				

Acknowledgment

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Vapor-Phase Catalytic Oxidation of Organic Compounds

TOLUENE

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The catalytic activity of various mixtures and compounds was investigated in the vapor-phase oxidation of toluene to produce benzaldehyde and benzoic acid. Results on sixteen catalysts which showed an appreciable effect are reported. The temperature, concentration of vapor, and time of contact were varied over a wide range with each catalyst. The best results were obtained with a mixture of uranyl molybdate and boron carbide at a temperature of 575° C., space velocity (primary air) 420, space velocity (secondary air) 1010, air-hydrocarbon ratio 1.38 by weight, and volume of catalyst 19.3 cc.; the yield of benzaldehyde on the basis of toluene vaporized was 20 per cent per pass. The space velocities are expressed in terms of inlet air.

A brief discussion of this problem is given in the light of the results obtained from this investigation. A possible commercial application is suggested which greatly simplifies the apparatus and method of operation over that which has been previously suggested.

THE oxidation of aromatic compounds for the production of partially oxygenated derivatives has become of great industrial importance. Various substances which were formerly prohibitive in cost because of the complicated methods of production are now relatively cheap and abundant. An outstanding example is the manufacture of phthalic anhydride from the vapor-phase oxidation of naphthalene.

Several methods are employed in the production of benzaldehyde from toluene involving such processes as liquid-phase oxidation, hydrolysis of chlorinated toluene derivatives, and the partial combustion of toluene in the vapor phase. Notwithstanding the diversity in the methods of production, the cost of benzaldehyde (free from chlorine) is extremely high.

The purpose of this investigation was to determine the action of various catalysts in controlling the partial oxidation of toluene in the vapor phase. It was believed that the proper mixture of certain metallic oxides would result in a favorable yield of benzaldehyde. After a thorough search of the literature, the metallic oxides of the fifth and sixth groups were found to be the most effective in controlling this reaction. These substances, both singularly and in mixtures, were investigated for their catalytic properties. Various catalyst supports and promoters were also tried, and the change in partial oxidation with temperature, concentration, and time of contact was recorded.

The recognition of the fact that toluene may be partially oxidized in the vapor phase is relatively old. Coquillon (*6*) passed a mixture of benzene and toluene vapor with air through a tube containing incandescent platinum wire and found that benzaldehyde and benzoic acid were formed. He later reported that palladium was a better catalyst for the reaction than platinum. The vapor-phase oxidation of toluene was further investigated by Walter (*24*), the result of which was the important discovery of the catalytic properties of vanadium pentoxide. A comprehensive treatment of the partial oxidation of hydrocarbons was published by Orloff (*22*) in which he reported a 4 per cent yield of benzaldehyde on passing a mixture of toluene vapor and air over copper.

The influence of various metallic oxides such as those of nickel, manganese, and iron was investigated by Woog (*25*). Ferric oxide gave the best yield when the tube was heated to 280° C. and the toluene to 90° C. Coke gave excellent results in the oxidation of toluene to benzoic acid. The other substances were reported as giving mostly total oxidation products.

The field of vapor-phase oxidation of aromatic compounds became quite active following the work of Gibbs (*10*) on the oxidation of toluene. Later Gibbs and Conover (*11*) announced the production of phthalic anhydride by the vapor-phase oxidation of naphthalene, and the manufacture of maleic anhydride from benzene was announced by Weiss and Downs (*9*). Both processes were covered by patents. A great deal of information is to be found in the patent literature since 1917 concerning the most effective catalyst and the construction of apparatus for this purpose (*19*).

Kuznetzov and Stepanenko (*17*) investigated the catalytic activity of basic zinc manganate, vanadium pentoxide on asbestos and on pumice stone, molybdenum trioxide on asbestos, and bismuth vanadate on pumice stone. Molybdenum trioxide gave 11.1 per cent benzaldehyde when the temperature of the catalyst was 425° C., length of contact layer 24 cm., volume of air per hour 100 liters, and the temperature of vaporizing bath 63° to 65° C.

Chowdhury and Choudhury (*5*) reported an 18 per cent yield of benzaldehyde using reduced nickel oxide as a catalyst. Tin vanadate in the form of porous pills gave 14.1 per cent aldehyde at 450° C. The use of silica gel as a carrier improved the yield.

Numerous investigators (*4*) have published the results of their investigations on the vapor-phase oxidation of toluene and its derivatives in which one may find a comprehensive treatment of the catalytic activity of a number of metallic oxides and the different factors which influence this reaction.

Experimental Procedure

The oxidizing agent could be either air or pure oxygen. Air was used in this work for it was deemed advisable to adhere to industrial conditions as closely as possible. Also the presence of nitrogen acted as an excellent diluent.

Table I. Results with Various Catalysts

	Catalyst[a]	Primary Space Velocity[b]	Secondary Space Velocity[b]	Air-Hydrocarbon Ratio[c]	Vol. of Catalyst	Temp. of Reactor	O₂ Consumed in: Total oxidation	O₂ Consumed in: Partial oxidation
					Cc.	° C.	%	%
1.	$PbCr_2O_7$[d]	301	793	1.26	19.4	390	11.9	2.4
						400	16.7	7.1
						415	33.3	11.9
						435	74	21.4
						445	76.3	16.7
2.	$PbWO_4$[d]	294	788	1.25	19.4	350	4.8	2.9
						385	11.4	3.3
						420	73.3	21.9
						445	75.2	23.8
						495	76.2	21.9
3.	$Pb(VO_3)_2$[d]	257	688	1.27	22.5	360	16.7	5.7
						400	68	21.9
						440	77	22.8
						465	75.3	23.8
						495	76.8	21.9
						515	78.2	21.9
4.	$PbMoO_4$[d]	258	814	1.29	19.3	345	1.9	1.9
						445	7.1	4.8
						495	32.4	14.3
						545	64.3	27.6
						585	69	29.5
5.	UO_2WO_4[d]	395	1060	1.39	14.5	425	7.6	0
						445	7.8	4.8
						480	23.8	14.3
						505	39	21.4
						545	50.5	26.2
6.	$(UO_2)WO_4$[d] + Al_2O_3	395	1060	1.39	14.5	405	30.9	21.4
						445	40	21.4
						500	59	25.7
						545	62.8	28.8
7.	$UO_2MoO_4 + B_4C$[d]	228	611	1.29	25.8	375	48	0
						400	23.8	11.9
						425	41.9	21.9
						445	61.8	36
						475	58	39.1
						510	58	38.1
8.	$UO_2MoO_4 + B_4C$[d]	420	1010	1.38	19.3	445	16.7	16.7
						495	46.6	38.1
						575	53.3	45
9.	$UO_2MoO_4 + B_4C$[d]	420	1000	1.42	19.3	455	16.7	16.7
						495	46.6	38.1
						560	53.3	45
						585	53.3	45
10.	UO_2MoO_4 (no carrier)	414	..	1.6	65	350	0	0
						406	6.7	8.6
						430	15.2	12.4
						524	74.3	23.8
11.	U-Mo-B_4C (4-1-1)[e]	302	805	1.28	19.3	350	0	2.4
						365	0	2.4
						410	4.8	4.8
						455	28.8	12.4
						495	54.8	23.8
						540	64.3	31.4
						575	60	35.3
12.	U-Mo-B_4C (4-1-1)[e]	302	1392	1.95	19.3	350	2.4	5.7
						415	2.4	5.7
						465	14.3	11.9
						495	28.8	17.2
						540	47.6	29.5
						575	53.3	31
13.	U-Mo-B_4C (3-2-1)[e]	302	805	1.28	19.3	365	1.9	4.8
						410	4.8	9.5
						460	60	25.7
						535	65	35.2
						575	59	40
14.	U-Mo-B_4C (3-2-1)[e]	302	1392	1.95	19.3	425	7.1	7.1
						470	35.7	23.8
						517	50	37.1
						575	54.3	42.9
15.	$U(MoO_4)_2$[d]	500	..	3.58	65	385	7.1	7.1
						400	16.7	10.5
						415	27.6	16.2
						450	68.6	29.5
						510	73.3	24.7
						553	77.2	21.9
						600	86.6	12.4
						650	69	29.5
						658	65.7	33.3
16.	$U(MoO_4)_2$[d]	492	..	6.33	65	390	15.2	8.6
						420	36.1	12.4
						470	75.3	16.2
						500	69	29.5
						535	72.5	26.7
						600	81	17.1

[a] Unless otherwise specified, the catalysts were supported on granular aluminum.
[b] Space velocity = liters of gas at S. T. P. in hours per liter of catalyst space.
[c] (Grams of air at S. T. P. per hour)/(grams toluene vaporized per hour).
[d] Made by precipitation from aqueous solution.
[e] Weighed as $UO_2(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and B_4C in the stated ratios.

The composition of the air-hydrocarbon mixture was controlled by changing the temperature of the vaporizing bath and thereby increasing or decreasing the toluene vapor content in the air current. It was found that under the conditions employed in this experiment Berthelot's equation for vapor pressure was not applicable. A blank for the quantity of toluene vaporized had to be run for each primary air flow. This was done by running the apparatus under the conditions to be employed but with no catalyst in the reaction tube. At the exit of the reaction tube the toluene was condensed out and measured. The volume of air passed was measured by calibrated flowmeters.

The reaction to form benzaldehyde and benzoic acid is highly exothermic (Equations 3 and 4); and since the heat of reaction (*16*) is greater than that necessary to heat the incoming mixture to the temperature of the catalyst chamber, good heat transfer is important.

The reaction chamber (*7*) was constructed by welding fourteen-gage steel to form a U (Figure 1) with a thin cross section 2 × 0.25 inches (5 × 0.635 cm.) inside diameter, the length from the side arm to the bottom of the U being 11 inches (27.9 cm.). Good heat conduction and a relatively large radiating surface per unit volume are the advantages of this unit.

Various substances were used as catalysts in this reaction. They were first tested in a smaller apparatus constructed especially for this purpose (Figure 2). If a mixture or compound was found favorably active, it was loaded in the large apparatus. Compounds of vanadium, molybdenum, uranium, tungsten, lead, chromium, silver, tantalum, and columbium were tried. Boron carbide and boron arsenate were also used.

The catalysts were prepared by standard methods as described in Mellor (*20*). Different substances were used as supports such as granular aluminum (*8*), pumice, asbestos, and alumina. The time of contact was controlled as far as possible by the temperature of the catalyst and the rate of flow of the gases.

The primary air supply was washed and dried in a standard gas train (Figure 3). It was then metered, preheated in glass coils, and bubbled successively through three vaporizing tubes containing toluene. The preheating coils and saturators were kept at a constant temperature by an automatically regulated oil bath. The mixture of air and vapor thus obtained was passed into the steel U-tube where the catalyst was suspended on granular aluminum. If an excess of air was required, a secondary air supply, purified in the same manner as the primary air and preheated to the temperature of the vaporizing bath, was admitted to the air-vapor mixture just before it entered the catalyst tube. The reaction tube was submerged in an electrically heated lead bath automatically controlled by an air thermoregulator (*15*). All temperatures were measured by calibrated thermocouples. A thermocouple extended into the catalyst mass to a depth of approximately 1.5 inches (3.8 cm.), and the temperature registered by this thermocouple is recorded in Table I as the temperature of the reactor. The exit gases

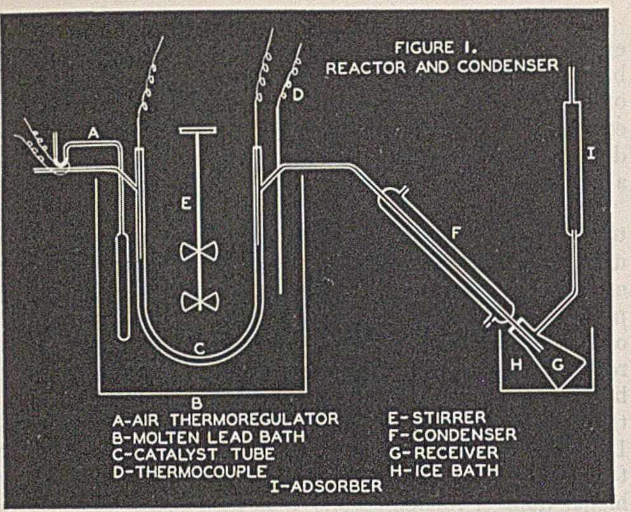


FIGURE 1. REACTOR AND CONDENSER

were condensed by a water-cooled coiled condenser connected to an ice bath and finally a charcoal scrubber to remove uncondensed toluene vapor. The length of a run varied from 2 to 4 hours, usually until 100 cc. of drip were collected.

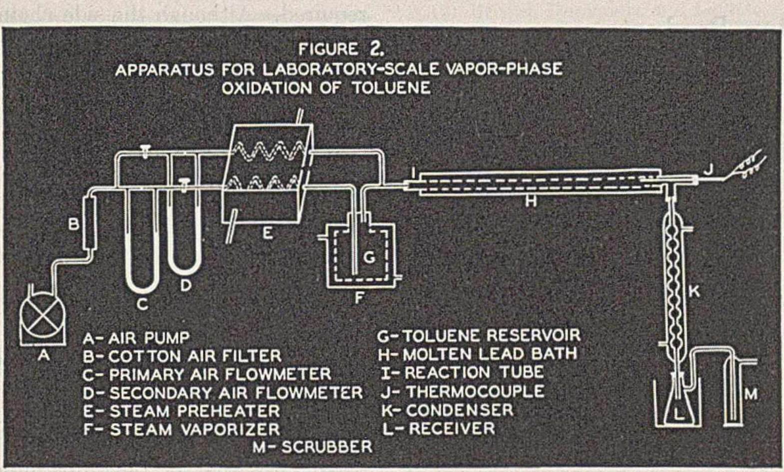


FIGURE 2. APPARATUS FOR LABORATORY-SCALE VAPOR-PHASE OXIDATION OF TOLUENE

The gaseous products of the reaction were analyzed by means of an Orsat apparatus. The liquid drip was analyzed as follows:

The water layer was determined by the physical boundary in a graduated cylindrical flask. Twenty cubic centimeters of the oil layer in the drip were shaken with saturated sodium disulfite solution, and the precipitate was dried and weighed. Another 20 cc. were treated with dilute sodium carbonate solution, then with sulfuric acid, and finally extracted with ether. The ether was allowed to evaporate at room temperature, and the benzoic acid crystals were weighed. These analyses were not carried out in all cases so that analytical data on benzaldehyde and benzoic acid are not reported. The reaction with the different catalysts was followed by gas analysis and, when the results appeared promising, the chemical analysis was carried out. Therefore, the results of the gas analysis are reported, and only the maximum yield of benzaldehyde and benzoic acid is given. No products other than the benzaldehyde and benzoic acid were determined, although the formation of anthraquinone, a yellow oil, and a brown gummy material was noted with some catalysts. The amount of anthraquinone formed was very small and seemed to be favored by the uranium catalysts. The pure benzoic acid was removed from the drip by water extraction and then crystallization. After the water extraction the disulfite reaction was used to remove the benzaldehyde. The remaining liquid was distilled to recover unreacted toluene for recirculation.

Effect of Various Catalysts

The results obtained with the various catalysts are given in Table I, and representative examples have been plotted from these data. No change for primary or secondary space velocities are reported for the various temperatures for the same catalyst. It is realized that, as the gases undergoing reaction increase in temperature, their volume increases and the time of contact is reduced, and therefore the space velocities might better be based on the temperature and pressure prevailing while the gases are passing through the voids in the catalyst mass. However, in these results the pressure is not important; the laborious temperature calculations have been avoided and the data are reported in the customary manner. Other catalysts employed were $Cr_2O_3 \cdot WO_3$, B_4C, NH_4MoO_4, $HMoO_3$, $UO_2(NO_3)_2 \cdot 6H_2O$, U-Mo-Ag-B_4C, Ta-Cb-U, and $Co(NH_3)_6(VO_3)_3$. No data are reported for these catalysts because the Ta-Cb-U mixture was very poor while the others were only fair and may be classified with respect to partial oxidation at optimum conditions as similar to catalyst 5 in Table I. In connection with catalyst 15 it is interesting to note that the entire mass fused and had to be drilled out. Often at lower temperatures the aluminum would pulverize or the edges would melt, undoubtedly because of the formation of hot spots.

It was thought that the lead derivatives of the metals of the fifth and sixth groups of the periodic system would favor partial oxidation of the side chain since tetraethyllead slows down the rate of oxidation of gasoline. Lead dichromate, tungstate, vanadate, and molybdate were used (Figure 4); the highest partial oxidation with these lead catalysts was 29.5 per cent of the available oxygen at 585° C. with lead molybdate. These curves show that the quantity of oxygen consumed in total oxidation is usually in excess of that in partial oxidation and that they tend toward an inverse curve. Although we would expect total oxidation at high temperatures (600° C.), this reaction did not take place with any of the substances employed. A catalyst favorable to partial oxidation remains so at almost any reasonable temperature and concentration of the vapor.

The effect of increasing the oxygen supply and decreasing the time of contact simultaneously is shown in Figure 5. The change resulted in a lower carbon dioxide content and an increase in the yield of partially oxidized compounds. This mixture of uranyl molybdate and boron carbide supported on granular aluminum gave, besides benzaldehyde and benzoic acid, anthraquinone, a light yellow oil of pungent odor,

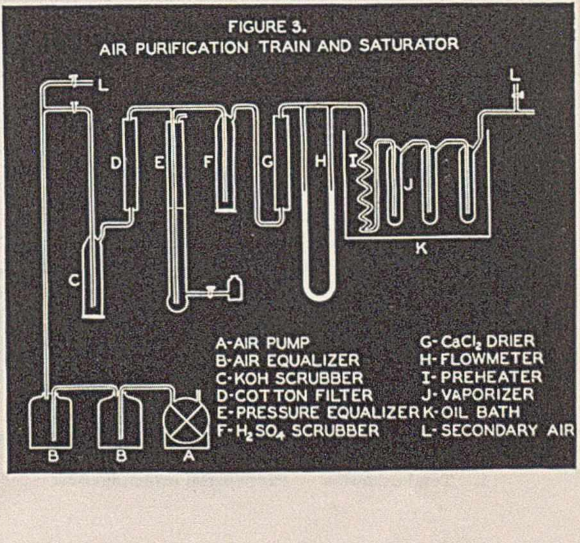


FIGURE 3. AIR PURIFICATION TRAIN AND SATURATOR

and a dark brown gummy material (*18*). At high temperatures small quantities of anthraquinone were formed with all catalysts. The presence of uranium and molybdenum increased this formation. With a primary space velocity of 420, a secondary space velocity of 1010, air-hydrocarbon ratio of 1.38 by weight, volume of catalyst 19.3 cc., and a temperature of 575° C., a yield of 20 per cent by weight of benzaldehyde and 1.5 per cent benzoic acid per pass was obtained. This catalyst proved to be the best of all that were investigated.

Aluminum, pumice stone, asbestos, and aluminum oxide were used as supports; since the granular aluminum was the best heat conductor, it decreased the formation of hot spots and thereby lowered the total oxidation and increased the partial oxidation (Figure 6).

A series of runs was made with uranium molybdate as a catalyst in which all the independent variables were kept constant except the temperature of the vaporizing bath. The effect caused by the change in concentration of the toluene vapor was not as might be expected. The total oxidation per weight of toluene vapor remained fairly constant and appeared to be a specific property of the catalyst employed.

Oxidation Products

There are five products of oxidation which may be expected from this reaction:

$$C_7H_8(l.) + {}^1/_2O_2 = C_6H_5CH_2OH(l.) + 39{,}900 \text{ cal.} \quad (1)$$

$$C_7H_8(l.) + O_2 = C_6H_5CHO(l.) + H_2O(l.) + 91{,}200 \text{ cal.} \quad (2)$$

$$C_7H_8(l.) + {}^3/_2O_2 = C_6H_5COOH(s.) + H_2O(l.) + 156{,}300 \text{ cal.} \quad (3)$$

$$C_7H_8(l.) + 6O_2 = C_4H_2O_3(s.) + 3CO_2 + 3H_2O(l.) + 600{,}300 \text{ cal.} \quad (4)$$

$$C_7H_8(l.) + 9O_2 = 7CO_2 + 4H_2O(l.) + 934{,}400 \text{ cal.} \quad (5)$$

Benzyl alcohol has not as yet been isolated as one of the products of partial oxidation at atmospheric pressure, although Bone (*1*) reports the formation of alcohol to the extent of 16 per cent of the toluene partially oxidized under a pressure of 50 atmospheres.

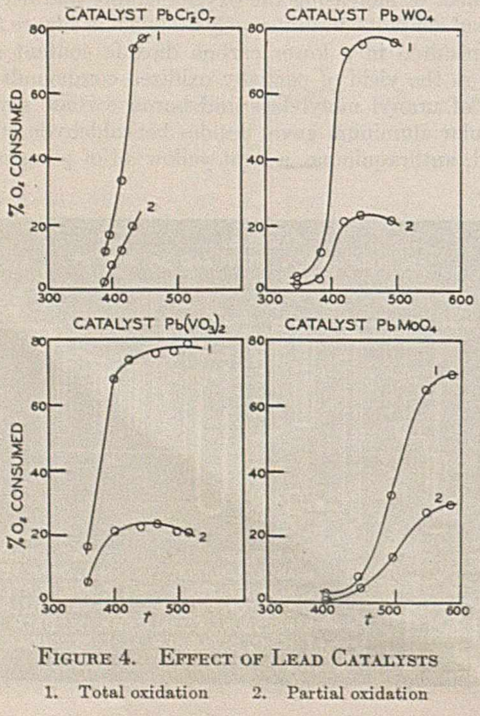


FIGURE 4. EFFECT OF LEAD CATALYSTS

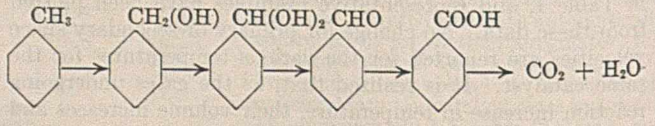
1. Total oxidation 2. Partial oxidation

The oxidation of toluene to maleic anhydride is highly exothermic. At high temperatures the added heat of combustion (151,900 calories) due to the attached methyl group on the benzene ring is enough to cause the destruction of the entire molecule if not removed as liberated. This is difficult to accomplish and is proved by the fact that no appreciable yield has been reported.

The stability of toluene (*23*) decreases with increase in temperature such that above 850° K. it is thermodynamically unstable with respect to the elements. Consequently in these experiments no temperature approaching this value was employed. In the presence of oxygen an even lower temperature of decomposition might be expected. The theoretical air required for the oxidation of a mole of toluene to benzaldehyde is 120 liters at 20° C. This toluene-air mixture lies on the rich side of the explosive limit as reported by Briand, Dumanois, and Laffitte (*2*) and is therefore relatively safe to employ. It is interesting to note from their data that the higher limit of inflammability is not a straight line at temperatures above 200° C., but the percentage of toluene decreases rather than increases as would be expected. This allows even one-half the theoretical amount of air to be used for exceptionally lean mixtures if very mild conditions are required. Although the side chain of toluene is aliphatic, it is much more stable toward oxidation than the paraffin hydrocarbon. Once the maximum partial oxidation has been reached, variations in temperature as high as 50° C. do not materially affect the yield. It is easily seen that a low concentration of oxygen and relatively high temperatures should favor the formation of benzaldehyde, whereas excess oxygen and low temperatures should favor the production of benzoic acid. This is true of catalysts that are capable of forming both and has been reported to be the case by Chowdhury and Choudhury (*5*).

The increased activity of mixtures of metallic oxides may be due to structural changes in the crystal lattice (*12*). As most of these mixed oxides were made by precipitation from aqueous solutions, the lattice structure of the pure substance may be altered by the presence of the foreign substance. These internal changes should produce a change in reactivity compared with that of the fully uniform crystal. Several investigations of such cases have proved the correctness of this hypothesis (*13*). Huttig (*14*) was able to use this theory in explaining the change in catalytic activity observed during the aging period of the catalyst.

The theory of hydroxylation which proposes that the oxidation takes place through the successive formation of hydroxylated compounds explains the mechanism of the reaction with the most satisfaction. For this reaction to take place it is necessary to have atomic oxygen. The substances which have been found favorable toward partial oxidation are members of the "gap elements" and are capable of having various valences. The colors of a catalyst when removed from the reaction chamber show these various stages of oxidation. This behavior leads us to the conclusion that these compounds are alternately oxidized by the air and reduced by the toluene, atomic oxygen being liberated each time. The temperature at which these catalysts become active is usually that point at which this oscillating effect takes place. The reaction is believed to be as follows:



The possibility of the reaction through activated molecular oxygen,

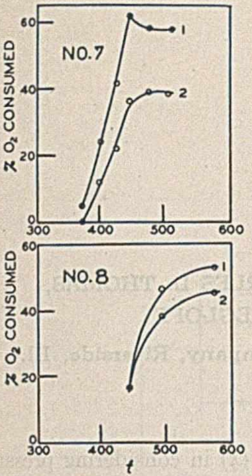


FIGURE 5. EFFECT OF INCREASING OXYGEN SUPPLY AND DECREASING CONTACT TIME

1. Total oxidation
2. Partial oxidation

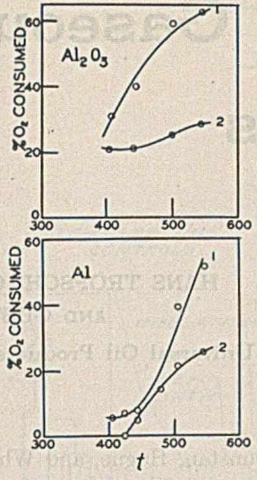
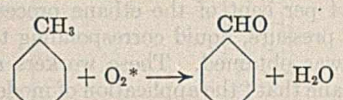


FIGURE 6. EFFECT OF CATALYST SUPPORT ON OXIDATION WITH URANYL TUNGSTATE

1. Total oxidation
2. Partial oxidation



is doubtful, for the energy of activation is extremely high and it is hard to see from whence this sum is available; the heat of adsorption or condensation is hardly enough to foster this reaction.

Newitt and Szego (*21*) report the formation of hydroxylated compounds using a temperature of 210° C. and a pressure of 50 atmospheres. About 60 per cent of the toluene burned appeared as hydroxy derivatives, which consisted of benzyl alcohol, a small quantity of benzaldehyde, 2, 4-dihydroxytoluene, and benzoic acid. The formation of benzyl alcohol and 2, 4-dihydroxytoluene shows that the aromatic nucleus and the aliphatic side chain may be simultaneously oxidized.

Commercial Possibilities

The data recorded in this paper show that the catalysts employed reached a point of maximum activity, both in respect to partial and total oxidation, at a definite temperature and remained almost constant over a range of 50° to 75° C. If approximately one-half the theoretical amount of air required to oxidized toluene to benzaldehyde was used, the maximum partially oxidized compounds would be about 20 per cent per pass and about 30 per cent sacrificed to carbon dioxide and water. This yield would make the concentration of the aldehyde in the drip workable for the commercial production of benzaldehyde, and the expensive and complicated converters for precise temperature control would be avoided provided such a catalyst as uranyl molybdate plus boron carbide was used.

The authors believe that this reaction could be carried out commercially with an apparatus of moderate cost. The compressed air could be purified and preheated, and then passed through a steam jacketed toluene vaporizer, or the liquid toluene may be injected before the air enters the catalyst chamber. The mixture of air and toluene vapor then enters a metal coil where it is heated to the temperature of reaction (500° C.). The gases are then passed into the catalyst chamber which consists of a steel cylinder 1 foot (0.3 meter) in diameter and about 3 feet (0.9 meter) in height containing two layers of catalyst supported on granular aluminum. The heat generated by total oxidation would not be enough to raise the temperature of the incoming gases 50° C., but to be on the safe side a cooling device may be installed between the catalyst layers. A somewhat similar arrangement has been suggested for the production of phthalic anhydride from naphthalene (*3*). The high-boiling fraction could be condensed by water-cooled coils and the remaining toluene mixture scrubbed with bisulfite solution. This arrangement would simplify the apparatus as now suggested by most authors.

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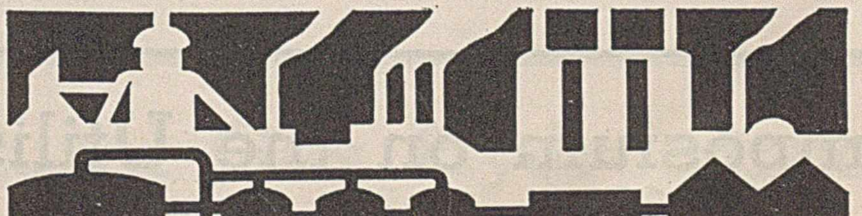

Pressure Pyrolysis of Gaseous Paraffin Hydrocarbons

Propane, n-butane, isobutane, and mixtures containing these gases were pyrolyzed at 525° to 575° C., and at 51 kg. per square cm. (725 pounds per square inch) pressure. The gases produced contained paraffin hydrocarbons of lower molecular weight than the hydrocarbon charged, along with ethylene, propene, and butenes. At a sufficiently long contact time a part of the olefins was pyrolyzed to liquid products. By catalytically polymerizing the olefins liquids were produced; it is estimated that 1 cubic meter of butanes would give 1.5 liters of liquid product (11.5 gallons from 1000 cubic feet), 90 per cent of which is gasoline having an octane number of 77 or a blending value of 93 octane by the C. F. R. motor method.

HANS TROPSCH, CHARLES L. THOMAS,
AND GUSTAV EGLOFF
Universal Oil Products Company, Riverside, Ill.

⑧ IN ATTEMPTING to utilize the hydrocarbons in natural gas, the chemist has been handicapped by the inertness of these hydrocarbons. He has therefore adopted drastic methods of treatment to force them into reaction. One such treatment is the pyrolysis of these gaseous hydrocarbons under various conditions of time, temperature, and pressure to produce olefins, which are more reactive than the original paraffins, and at the same time liquid products. Egloff, Schaad, and Lowry (*5*) reviewed this type of work. The results of these pyrolyses have tempted investigators to study the commercial applicability of these processes (*1*, *2*, *12*). Frolich and Wiezevich (*8*) and Sullivan, Ruthruff, and Kuentzel (*13*) studied the utilization of the gaseous paraffin hydrocarbons by cracking them to olefins at atmospheric pressure and separately polymerizing at high pressures.

Davidson (*3*) working with an ethane-propane mixture at pressures up to 7 kg. per square cm. (100 pounds per square inch) and temperatures of 680° to 850° C., came to the conclusion that the pyrolysis took place in two steps: The first was the formation of an olefin and paraffin, and the second was the condensation of the olefins to form liquid products. The first step was considered to be hindered by pressure and the second favored thereby.

Dunstan, Hague, and Wheeler (*4*) in considering pressure effects state that "from theoretical considerations the application of pressure to the pyrolysis of paraffin hydrocarbons is not sound, for the initial reaction must involve an increase in volume." They give data to show that in the pyrolysis of ethane at 750° C. and 10.5 kg. per square cm. (150 pounds per square inch) the yield of liquid products formed corresponded to 12.4 per cent of the ethane processed, whereas at atmospheric pressure, liquid corresponding to 22 per cent of the ethane was obtained. These workers also conclude in regard to ethane that "the application of moderate pressure such as 3.5 kg. per square cm. (50 pounds per square inch) is sufficient to reduce considerably the olefin production and the quantity of aromatic hydrocarbons."

Evidently, therefore, there is some question as to whether the gaseous paraffin hydrocarbons can be effectively pyrolyzed under superatmospheric pressures. The purpose of this work is to give the results obtained by the pyrolysis of gaseous paraffins under pressures of from 17.5 to 70 kg. per square cm. (250 to 1000 pounds per square inch).

Theoretical Discussion

In the pyrolysis of hydrocarbons under pressure the application of the Le Chatelier principle to certain of the pyrolytic reactions taking place is questioned. It is granted that, where the reaction involved is reversible, the Le Chatelier principle is valid. For example, in the reaction $A \rightleftarrows B + C$, the application of pressure on the reacting system would favor the formation of A or suppress the decomposition of A into B and C. This situation is present in Dunstan, Hague, and Wheeler's experiments with ethane (*4*), for the principal pyrolytic reaction of ethane is

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

which is an equilibrium reaction. As far as ethane is concerned, these workers were correct when they stated that "the application of pressure to the pyrolysis of paraffinic hydrocarbons is not sound." However, in the pyrolysis of the paraffin hydrocarbons in the present study certain reactions take place which are not, so far as is known, reversible under the conditions of the experiments. Reactions 2, 5, 6,

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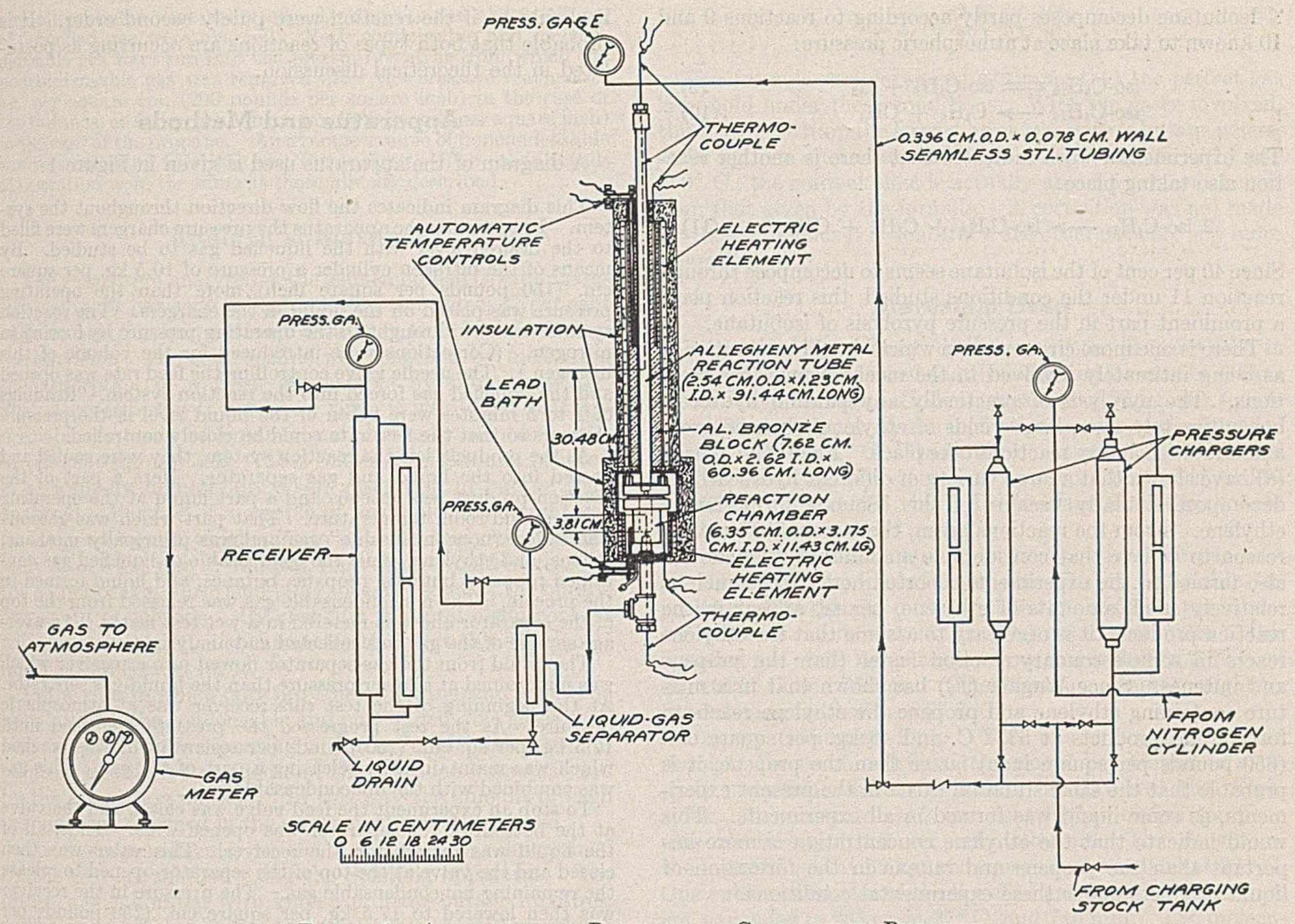

Figure 1. Apparatus for Pyrolysis of Gases under Pressure

etc., discussed later seem to be of this type. If it is true that these reactions are not reversible under the conditions studied, then it is improbable that the application of pressure would hinder these reactions.

The same reactions take place at increased pressure as at atmospheric pressure. With propane the following reactions take place at atmospheric pressure:

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \quad (1)$$

$$C_3H_8 \longrightarrow C_2H_4 + CH_4 \quad (2)$$

$$2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4 \quad (3)$$

Since reaction 2 is not an equilibrium one, it should not be influenced by the application of pressure, whereas reaction 1 should be suppressed. As pointed out by Frey and Smith (7), reaction 3 plays a very small role in the pyrolysis at atmospheric pressure but it will predominate more and more as the reaction pressure is increased. This effect is to be expected since the reaction is bimolecular and the rate of a bimolecular reaction is proportional to the concentration of the substance undergoing change.

With n-butane at atmospheric pressure the principal reactions are:

$$n\text{-}C_4H_{10} \rightleftharpoons n\text{-}C_4H_8 + H_2 \quad (4)$$

$$n\text{-}C_4H_{10} \longrightarrow C_3H_6 + CH_4 \quad (5)$$

$$n\text{-}C_4H_{10} \longrightarrow C_2H_4 + C_2H_6 \quad (6)$$

According to Neuhaus and Marek (*11*), reactions 5 and 6 account for 48.5 and 34.5 per cent, respectively, of the reaction products at 600° C. and atmospheric pressure. These reactions would not be changed by the application of pressure. Reaction 4 accounts for 16 per cent of the products at atmospheric pressure and would be suppressed by increasing pressure.

In addition to these reactions two are proposed which probably play an important part in the pressure reactions observed in this work. They are:

$$2n\text{-}C_4H_{10} \longrightarrow n\text{-}C_4H_8 + C_3H_8 + CH_4 \quad (7)$$

$$2n\text{-}C_4H_{10} \longrightarrow n\text{-}C_4H_8 + 2C_2H_6 \quad (8)$$

It is indicated in the experimental work that about 30 per cent of the reacting n-butane decomposes through reaction 7, whereas less than 5 per cent decomposes through reaction 8. Of the two equations, 7 is the more important under the conditions studied.

# of Natural Gas Hydrocarbons

at the 90th Meeting of the American Chemical Society, San Francisco, California, August 19 to 23, 1935.

Isobutane decomposes partly according to reactions 9 and 10 known to take place at atmospheric pressure:

$$\text{iso-C}_4\text{H}_{10} \rightleftharpoons \text{iso-C}_4\text{H}_8 + \text{H}_2 \qquad (9)$$

$$\text{iso-C}_4\text{H}_{10} \longrightarrow \text{C}_3\text{H}_6 + \text{CH}_4 \qquad (10)$$

The experimental work indicates that there is another reaction also taking place:

$$2\ \text{iso-C}_4\text{H}_{10} \longrightarrow \text{iso-C}_4\text{H}_8 + \text{C}_3\text{H}_8 + \text{CH}_4 \qquad (11)$$

Since 40 per cent of the isobutane seems to decompose through reaction 11 under the conditions studied, this reaction plays a prominent part in the pressure pyrolysis of isobutane.

There is one more circumstance which should be mentioned as being intimately involved in the mechanism of the reactions. The pyrolysis of practically any paraffin hydrocarbon ultimately gives large yields of ethylene when no great amount of secondary reactions take place. Egloff and Wilson (*6*) have shown that a large variety of different hydrocarbons decompose similarly because of this common formation of ethylene. From the reactions given, there seems to be every reason to believe that considerable amounts of ethylene are also formed in the experiments reported here. Inasmuch as relatively small amounts of ethylene, per se, appear in the reaction products, it is necessary to assume that the ethylene reacts in some secondary reaction faster than the propene and butenes. Since Wagner (*14*) has shown that in a mixture containing ethylene and propene the ethylene reacts to form liquid products at 537° C. and 46 kg. per square cm. (650 pounds per square inch) faster than the propene, it is probable that the same situation exists in the present experiments, as some liquid was formed in all experiments. This would indicate that the ethylene concentration is more important than the propene and butene in the formation of liquid products under these experimental conditions.

Kinetics

In the present work where the effect of pressure was studied, the reaction velocity constants for the rate of disappearance of the paraffin hydrocarbons in the gas charged have been calculated for both first- and second-order reactions. For the first-order constant (K_1) the reaction velocity constant was calculated from the equation:

$$K_1 = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

For the second-order rate constant (K_2) the reaction velocity constant was calculated from the equation:

$$K_2 = \frac{1}{t} \frac{x}{a(a - x)}$$

In both of these equations t is the reaction time in minutes (contact time), a is the original concentration of the reacting substance, and x is the part of the original substance which has reacted at the end of time t (the concentrations are in gram moles per liter). Thus $a - x$ was taken to be the concentration of the paraffins remaining undecomposed in the condensable gas. Since these recovered paraffins usually contain some paraffins of molecular weight lower than the molecular weight of the original hydrocarbons, it follows that the value for $a - x$ is not quite correct, since it is too large. The error involved depends somewhat on the individual experiment. For this reason there is some variation in the constants which would otherwise be absent. The constants are given at the foot of Table V. The increase in reaction velocity with increasing pressure indicates that the reaction is not purely first order. According to the second-order rate constants the reaction rate is not increased nearly as much as it should be if the reaction were purely second order. It is probable that both types of reactions are occurring as postulated in the theoretical discussion.

Apparatus and Methods

A diagram of the apparatus used is given in Figure 1:

This diagram indicates the flow direction throughout the system. In operating the apparatus the pressure chargers were filled to the desired level with the liquefied gas to be studied. By means of the nitrogen cylinder a pressure of 10.5 kg. per square cm. (150 pounds per square inch) more than the operating pressure was placed on the liquid in the chargers. The reaction system was then brought to the operating pressure by forcing in nitrogen. (Corrections were introduced for the volume of this nitrogen.) The needle valve controlling the feed rate was opened and the liquefied gas forced into the reaction system. Readings of 1 to 5 minutes were taken of the liquid level in the pressure chargers so that the feed rate could be closely controlled.

As the products left the reaction system, they were cooled and passed into the liquid and gas separator. Here a part of the reaction product was gaseous and a part liquid at the operating pressure and room temperature. That part which was gaseous was called "noncondensable" gas and was principally methane, ethane, and ethylene, while the condensable or liquefied gas contained propene, butenes, propane, butanes, and liquid formed in the process. The noncondensable gas was released from the top of the separator and was metered in a wet test meter. An average sample of the gas was collected and analyzed.

The liquid from the gas separator flowed into a receiver which was maintained at a lower pressure than the liquid-gas separator. At the beginning of the test this receiver was at atmospheric pressure. As the test progressed the pressure increased until 17.5 kg. per sq. cm. (250 pounds per square inch) was reached which was maintained by releasing a part of the gas. This gas was combined with the noncondensable gas.

To stop an experiment the feed valve was closed and the valve at the bottom of the separator was opened wide. Thus, all of the liquid was forced into the receiver. This valve was then closed and the valve at the top of the separator opened to release the remaining noncondensable gas. The pressure in the receiver was then lowered to 17.5 kg. per square cm. (250 pounds per square inch) by opening the valve at its top.

At the end of the run the receiver contained the condensable gas as a liquid with the space above the liquid filled with noncondensable gas. Knowing the volume occupied by this gas and the pressure on the receiver, the volume of noncondensable gas in the receiver could be calculated and the total volume of gas corrected accordingly.

A sample of the condensable gas was taken from the bottom of the receiver for analysis. The remainder of the gas was then released from the top of the receiver through the same wet test meter that was used for the noncondensable gas. (The same correction that was added to the noncondensable gas above was subtracted from the volume of condensable gas.) Releasing this pressure caused the liquefied condensable gas to boil so that the remaining liquid and the receiver were cooled to 5–10° C. This cooling prevented any appreciable amounts of the gasoline from being vaporized. The gasoline was stabilized by heating to 38–40° C. and then weighed.

The following combination Podbielniak and absorption analysis from a typical run is given to indicate the composition of the noncondensable and condensable gases and the degree of separation that was obtained (run G, *n*-butane charged):

Gas	Noncondensable Gas	Condensable Gas	Gas	Noncondensable Gas	Condensable Gas
	Per cent by volume			*Per cent by volume*	
H_2	2.5	0.0	C_3H_6	8.3	12.7
CH_4	48.2	3.2	C_3H_8	4.3	7.7
C_2H_4	4.8	1.7	n-C_4H_8	5.5	7.8
C_2H_6	16.6	9.8	n-C_4H_{10}	9.8	57.1

When the pure hydrocarbons were studied to obtain data on the reaction mechanism, a slightly different technic was used. The apparatus was filled to 51 kg. per square cm. (725 pounds per square inch) with nitrogen and the liquefied hydrocarbon was then forced in. The feed rate was adjusted, and a preliminary run of some 20 minutes was made during which all products were discarded. The apparatus was then placed "on stream" and all products were collected. During the run about 700 cc. of liquefied gas were charged. Both condensable and noncondensable gas were run into the pressure receiver from which the noncondensable gas was removed after the pressure reached 14 kg. per square cm. (200 pounds per square inch) in the case of the butanes, or 21 kg. per square cm. (300 pounds per square inch) in the case of the propane. An average sample of noncondensable gas was collected from the exit for analysis. The other details of operation were the same as those already described.

Analytical Methods

The gases were analyzed in the usual modified Orsat apparatus, using 63 per cent sulfuric acid for isobutene, 87 per cent sulfuric acid for propene and *n*-butenes, and bromine water for ethylene. The total olefins were checked by measuring the absorption of a fresh gas sample by bromine water. Such a procedure was necessary since it was found that appreciable amounts of butanes are physically soluble in the 87 per cent sulfuric acid. This solubility of butanes resulted in abnormally high results when gases rich in butane were analyzed. Further, if a sample of low-molecular-weight gas (average molecular weight, 20 to 25) was analyzed immediately after a gas rich in butanes, the volume would increase in the 87 per cent sulfuric acid pipet, because some of the butane comes out of solution. By checking the total olefin content with bromine water, it was possible to detect this solution of butanes and correct for it.

In the runs in which pure propane, *n*-butane, and isobutane were studied, the condensable and noncondensable gases were also analyzed by fractionating with the Podbielniak low-temperature distillation method and the fractions were analyzed by the absorption method. In this way the amount of each individual gas formed in the experiment was determined.

The average molecular weight of the gases was determined by the effusion method using the Schilling apparatus. The orifice was calibrated with known propane-butane mixtures.

The weight of gas charged was calculated from the volume read from the pressure chargers and the density of the liquid. This density was determined by filling the pressure charger as if a run were to be made. The gas was released from the feed valve into the calibrated wet test meter and then into a tared condenser-receiver combination, kept in a mixture of dry-ice and acetone. From 200 to 300 cc. of liquid were run out of the pressure chargers. In this way the volume of the liquid charge, the volume of the gaseous charge, and the density of liquefied charge under operating conditions could be determined.

From the molecular weight and volume of the gaseous products, and the weight of the liquid formed, it was possible to calculate the weight of the reaction products. From the volume and density of the liquefied charge, it was possible to find the weight of the charge. With these data, weight balances between input and exit weights were made to serve as a check on the analytical methods and also on minute leaks in the apparatus which otherwise might pass unnoticed.

The contact time (C. T.) was calculated by means of the following equation:

$$\text{C. T.} = V_r \times 60t \times \frac{273}{T} \times P \times \frac{2}{V_1 + V_0}$$

where V_r = vol. of apparatus at reaction temp., cc.
t = total time of experiment, min.
P = operating pressure, atm.
V_1 = vol. under standard conditions of gas charged to apparatus in time t, cc.
V_0 = vol. under standard conditions of gas and vapor recovered from apparatus in time t, cc.
T = abs. temp.

When V_r = 140 cc. and the pressure is 51 kg. per square cm. (725 pounds per square inch), the formula becomes:

$$\text{C. T.} = \frac{2.28 \times 10^8 t}{T(V_1 + V_0)}$$

This formula was developed assuming that the perfect gas laws hold under these conditions. With the gases involved, this is nearly true; the largest error was with *n*-butane where, at 70 kg. per square cm. (1000 pounds per square inch) and 550° C., the contact time is actually about 5 per cent longer than that given by the formula. A correction was not made for this error since it is doubtful if the other data are any more accurate.

Materials Used

PROPANE. A fractional distillation of the propane used in these experiments showed that it contained 2 per cent ethane as the only impurity. Under a pressure of 62 kg. per square cm. (880 pounds per square inch) the density of the liquefied gas was 0.49 at 24° C. One cubic centimeter of the liquefied gas under 62 kg. per square cm. pressure expanded to 297 cc. at 24° C. and 750 mm. The average molecular weight by the Schilling method was 42.5.

COMMERCIAL BUTANES. This gas contained 80 per cent *n*-butane and 20 per cent isobutane with no detectable impurities. The density of the liquefied gas at 62 kg. per square cm. pressure was 0.59 at 24° C. One cubic centimeter of this liquefied gas at 62 kg. per square cm. expanded to 257 cc. of gas at 24° C. and 750 mm. The average molecular weight by the Schilling method was 57.7.

BUTANE COMBINED FEED. This was a mixture made to simulate the combined feed that would be charged in a recycle operation where the butane mixture was the virgin stock. It contained 13.2 per cent higher olefins (propene plus butene) and 1.2 per cent ethylene. The density of the liquefied gas at 62 kg. per square cm. was 0.59 at 27° C. One cubic centimeter of the liquefied gas at 62 kg. per square cm. expanded to 283 cc. at 27° C. and 745 mm. The molecular weight by the Schilling method was 52.0. This gas was equivalent to 60 parts of condensable gas or recycle stock from the treatment of the butanes plus 40 parts of fresh butanes.

n-BUTANE. No other constituent was found in this C. P. *n*-butane from the Philgas Company, Kaw, Okla.

ISOBUTANE. This was C. P. isobutane from the Shell Company of California. The gas contained 98.1 per cent isobutane and 1.9 per cent *n*-butane.

NATURAL GAS FRACTION. The natural gas fraction when analyzed by the Podbielniak fractional distillation method showed the following:

Gas	Volume Per Cent
Air + methane	2.5
Propane	5.7
Isobutane	13.0
n-Butane	50.5
Pentanes	28.3

The density of the liquefied gas at 62 kg. per square cm. pressure was 0.557 at 27° C. One cubic centimeter of this gas at 62 kg. per square cm. expanded to 232 cc. at 27° C. and 745 mm. The molecular weight of the gas by the Schilling method was 60.

CONDENSABLE GAS OR RECYCLE STOCK. In pyrolyzing the natural gas fraction, the condensable gas could be recovered for recycling. Instead of actually making this recovery, a synthetic condensable gas or recycle stock having the same composition was prepared. The gas was used to show the effect of continuing the pressure pyrolysis of the condensable gas after the noncondensable gas and liquid products from the first reaction cycle had been removed. The density of the liquefied gas at 62 kg. per square cm. was 0.573 at 27° C. One cubic centimeter of the liquefied gas at 62 kg. per square cm. expanded to 265 cc. at 27° C. and 760 mm. The gas

TABLE I. PYROLYSIS OF PROPANE, *n*-BUTANE, AND ISOBUTANE AT 51 KG. PER SQUARE CM. (725 POUNDS PER SQUARE INCH)

	Propane				*n*-Butane				Isobutane	
Run No.	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
Continuous time, sec.	95.0	144.0	52.5	86.8	99.0	173.0	82.3	47.0	51.0	86.5
Temp., ° C.	555	555	585	585	525	525	555	555	555	555
Charge:										
Liters gas	201.0	208.0	207.0	216.0	199.0	176.5	186.0	180.0	176.0	146.3
Liters decomposed	26.2	36.5	44.5	86.0	51.0	68.0	103.0	78.0	38.0	37.7
Products, liters per 100 liters decomposed:										
H_2	6.1	4.9	9.8	6.6	1.5	1.9	2.2	0.0	5.5	6.4
CH_4	48.4	50.5	83.5	57.9	35.1	58.5	52.5	52.2	45.8	42.2
C_2H_4	25.2	32.3	27.8	16.3	12.5	6.9	7.4	10.3	2.9	4.5
C_2H_6	36.3	20.5	20.5	30.8	45.8	29.5	30.6	27.7	1.3	5.0
C_3H_6	32.4	28.8	35.6	23.5	18.2	21.3	25.1	31.0	37.1	38.5
C_3H_8	...	...	...	...	19.6	16.7	14.4	13.1	19.2	20.7
n-C_4H_8	...	...	...	...	23.2	18.3	17.8	16.6	...	...
Iso-C_4H_8	...	...	...	...	...	...	...	...	20.3	20.9
Liters of charge recovered unchanged	174.8	171.5	162.5	130.0	148.0	108.5	83.0	102.2	138.0	108.8
Liquid:										
Liters per cu. meter charged	0.013	0.053	0.067	0.12	0.10	0.17	0.29	0.71	0.04	00.53
Gal. per M cu. ft. charged	0.1	0.4	0.5	0.9	0.75	1.3	2.2	1.3	0.3	0.4

contained 22 per cent higher olefins (propene plus butene) and 1.6 per cent ethylene, and had an average molecular weight of 52 as determined by the Schilling method.

Pyrolysis of Propane, n-Butane, and Isobutane

In order to determine the reactions taking place during the pyrolysis of paraffin hydrocarbon gases under pressure, a number of experiments were made with pure propane, *n*-butane, and isobutane. As explained in the section on analytical methods, the gaseous products were analyzed by the low-temperature Podbielniak fractionation of the gases and then absorption analyses of the fractions. These methods give the amount of each gaseous hydrocarbon produced. Unfortunately the fractionation was not as close as could be desired in some instances, resulting in abnormal values. For this reason two to four runs were made with each gas and the yields averaged. All of the runs made are given in Table I. The yields of products have been converted into liters per 100 liters of original hydrocarbon reacted. From these data it is possible to determine the reactions taking place and the amount of original hydrocarbon converted through each reaction.

Since propane seems to follow reactions 1, 2, and 3, the extent of each reaction may be calculated from the number of liters of product formed when 100 liters of original hydrocarbon decompose. Thus, the number of liters of hydrogen per 100 liters of propane decomposed indicates the number of liters of original hydrocarbon decomposing through reaction 1. Similarly, the number of liters of methane less the number of liters of ethane indicates the number of liters of original hydrocarbon decomposing through reaction 2. Also, twice the number of liters of ethane indicates the extent of reaction 3. Since the calculations are based on 100 liters of original hydrocarbon decomposed, the values obtained are also the percentage of the original hydrocarbon decomposing according to the designated reaction.

Making the calculations indicated, the following values are obtained:

Per Cent Propane Reacting through:	Run				
	A	*B*	*C*	*D*	Av.
Reaction 1	6.1	4.9	9.8	6.6	6.8
Reaction 2	12.1	30.0	63.0	27.1	33.0
Reaction 3	72.6	41.0	41.0	61.6	54.0
Total	90.8	75.9	113.8	95.3	93.8

While some of the differences are quite large because of the gas analytical difficulties, it may be indicated that about 7 per cent of the propane decomposes through reaction 1, 33 per cent through reaction 2, and 55 per cent through reaction 3 under the conditions studied.

It must be pointed out that the yields of olefins are not nearly so reliable in determining the extent of the individual reactions as the paraffins because a part of the olefins may have disappeared through secondary reactions, forming liquid products. Liquid was formed in every experiment so that these reactions cannot be neglected. It is also possible that a part of the paraffins or hydrogen may have reacted in secondary reactions. In each case the most stable product available has been selected to represent the extent of the various reactions.

n-Butane seems to react through reactions 4, 5, 6, 7, and 8. Using the same type of reasoning applied to propane, it is found that the extent of the individual reactions may be determined as follows:

Per cent *n*-butane reacting through reaction 4 = liters H_2 per 100 liters *n*-butane reacted

Per cent *n*-butane reacting through reaction 5 = liters CH_4–C_3H_8 per 100 liters *n*-butane reacted

Per cent *n*-butane reacting through reaction 6 = liters C_2H_6–2-(*n* = C_4H_8–H_2–C_3H_8) per 100 liters *n*-butane reacted

Per cent *n*-butane reacting through reaction 7 = 2 × liters C_3H_8 per 100 liters *n*-butane reacted

Per cent *n*-butane reacting through reaction 8 = 2 × liters (*n* = C_4H_8–H_2–C_3H_8) per 100 liters *n*-butane reacted

Substituting the appropriate values from Table I gives the following:

Per Cent *n*-Butane Reacting through:	Run				
	E	*F*	*G*	*H*	Av.
Reaction 4	1.5	1.9	2.2	0.0	1.4
Reaction 5	15.5	41.8	38.1	39.1	33.6
Reaction 6	41.6	29.5	28.2	20.7	30.0
Reaction 7	39.2	33.4	28.8	26.2	31.9
Reaction 8	4.2	−0.6	2.4	7.0	3.2
Total	102.0	106.0	99.7	93.0	100.1

It has been necessary to resort to the yields of olefins in determining the extent of reactions 6 and 8 since there is no other simple way of obtaining the desired information. This is done with the full realization that the values so obtained may be considerably in error. Such an error probably accounts for the −0.6 value obtained in run *F* for reaction 8. Any correction for this error would result in a decrease in the extent of reaction 6 with a corresponding increase in reaction 8. From these data, reaction 4 accounts for about 1.5 per cent of the *n*-butane decomposed, reaction 5 for 33 per cent, reaction 6 for 30 per cent, reaction 7 for 32 per cent, and reaction 8 for 3.5 per cent under the conditions of these experiments.

Isobutane seems to decompose through reactions 9, 10, and 11. Small amounts of ethylene and ethane are also formed:

Per cent of isobutane reacting through reaction 9 = liters H_2 per 100 liters isobutane reacted
Per cent of isobutane reacting through reaction 10 = liters CH_4–C_3H_6 per 100 liters isobutane reacted
Per cent of isobutane reacting through reaction 11 = 2 × liters C_3H_6 per 100 liters isobutane reacted

The values obtained by means of these equations are as follows:

Per Cent Isobutane Reacting through:	Run *I*	Run *J*	Run Av.
Reaction 9	5.5	6.4	5.9
Reaction 10	37.1	38.5	37.8
Reaction 11	38.4	41.4	39.9
Total	81.0	86.3	83.6

The values given agree among themselves very well, but they do not add up to 100 per cent; further, the deficiency is too large to be ignored. It seems probable that about 5 per cent of the isobutane decomposes through the reaction which gives ethylene and ethane. The data indicate that about 6 per cent of the isobutane decomposed reacts through 9; 38 per cent through reaction 10; and 40 per cent through reaction 11 under the conditions studied.

It is significant that isobutane is much more stable under the conditions studied than *n*-butane. A comparison of runs *H* and *I* shows that isobutane at 555° C. gives 21.6 per cent decomposition in 51 seconds while *n*-butane at 555° C. gives 43.4 per cent decomposition in 47 seconds. Thus isobutane at 555° C. reacts only half as fast as *n*-butane.

These experiments (Table I) show that the hydrocarbons studied decrease in thermal stability in the order propane, isobutane, *n*-butane under the conditions used. In making these comparisons it was assumed that the stability is proportional to the time required to effect a given percentage decomposition at a given temperature.

Propane

In the preliminary experiments on cracking propane and butanes under pressure, it was found that 40 to 50 per cent of the gas charged could be decomposed and converted into liquid and gases of lower molecular weight in one pass through the apparatus. When a greater conversion than this was attempted, considerable coke was formed in the reaction chamber and more of the liquid product boiled above the gasoline range. With 40 per cent conversion or 60 per cent recovery as condensable gas, no coke deposition was noted.

With only 40 per cent of the gas charged converted per pass, or "once through" the apparatus, it is necessary to recycle the condensable gas recovered if the original gas is to be completely utilized. In recycle operation the 40 per cent decomposed would be replaced by fresh gas. Actual recycle studies were not made on the present small scale because of experimental difficulties, but data have been obtained which permit the estimation of the yields that would be obtained under recycle conditions. This is possible with gases because the recycle gas can be analyzed and the liquid yield from this material estimated from data already obtained.

The results obtained by pyrolyzing propane are summarized in Table II.

The noncondensable gas is that which was not liquefied in the separator while the condensable gas was liquefied. Of the data in Table II the yields of olefins and liquid are the most interesting. The calculated ultimate yields of these products from 1 cubic meter of propane by recycling operation are:

Runs No.	1	2
Noncondensable gas (CH_4 and C_2H_6), liters	950	1200 (olefin-free)
C_2H_4, liters	98	53
C_3H_6, liters	123	104
Liquid:		
Liters	0.2	0.21
Gal. per M cu. ft.	(1.5)	(1.6)

In calculating the olefin yields, it has been assumed that the olefins are removed from the condensable gas before recycling.

Table II. Pyrolysis of Propane at 51 Kg. per Square Cm. (725 Pounds per Square Inch) Pressure

Run No.	1	2
Temp., ° C.	550	575
Contact time, sec.	157	142
Propane charged, liters	581	790
Weight per cent of propane charged recovered as:		
Noncondensable gas	26.2	45.5
Condensable gas	67.6	45.2
Liquid product	2.6	6.7
Unaccounted loss	3.6	2.6
Liters noncondensable gas produced	240	543
In noncondensable gas:		
Vol. per cent C_2H_4	5.1	4.1
Vol. per cent C_3H_6	1.3	2.2
Liters C_2H_4	12.2	22.0
Liters C_3H_6	3.1	11.9
Av. mol. weight noncondensable gas	34.5	27.6
Liters of condensable gas produced	412	338
In condensable gas:		
Vol. per cent C_2H_4	1.7	1.2
Vol. per cent C_3H_6 + C_4H_8	5.1	11.8
Liters C_2H_4	7.1	4.0
Liters C_3H_6 + C_4H_8	20.9	40.0
Av. mol. weight of condensable gas	43.5	44.0
Liquid:		
Liters per cu. meter propane charged	0.067	0.13
Gal. per M cu. ft. propane charged	0.5	1.0
Liters C_2H_4 produced per cu. meter propane charged	33.1	33.2
Liters C_3H_6 produced per cu. meter propane charged	41.6	65.1
Liters C_3H_8 reacted per cu. meter propane charged	338	628

Table III. Pyrolysis of Commercial Butane at 51 Kg. per Square Cm. (725 Pounds per Square Inch) Pressure

	Commercial Butane			Butane Combined Feed	
Run No.	3	4	5	6	7
Temp., ° C.	550	550	550	537	550
Contact time, sec.	115	96	82	116	92
Butanes charged, liters	439	660	807	572	651
Products, weight per cent:					
Butanes charged recovered as noncondensable gas	28.7	20.6	17.4	13.7	23.1
Butanes charged recovered as condensable gas	58.3	64.4	70.6	67.0	58.0
Butanes charged recovered as liquid product	13.9	9.8	9.8	10.3	12.8
Butanes charged recovered as unaccounted loss or gain	−0.9	5.2	2.2	9.0	6.1
Liters noncondensable gas produced	292	295	309	165	310
In noncondensable gas:					
Vol. per cent C_2H_4	3.1	4.6	4.8	2.4	3.0
Vol. per cent C_3H_6	7.7	8.7	7.1	6.9	6.2
Liters C_2H_4	9.0	13.6	14.7	4.0	9.3
Liters C_3H_6	22.4	25.7	22.0	11.3	19.2
Av. mol. weight noncondensable gas	24.6	26.4	24.8	24.6	25.3
Liters condensable gas produced	296	497	617	408	403
In condensable gas:					
Vol. per cent C_2H_4	2.7	3.4	4.2	2.0	2.4
Vol. per cent C_3H_6 + C_4H_8	24.9	22.8	22.0	20.0	22.1
Liters of C_2H_4	7.9	17.0	26.0	8.2	9.6
Liters C_3H_6 + C_4H_8	73.5	113	137	81.7	89.0
Av. mol. weight condensable gas	49.3	49.0	50.6	49.0	48.7
Liquid:					
Liters per cu. meter butanes charged	0.41	0.31	0.31	0.29	0.35
Gal. per M cu. ft. butanes charged	3.1	2.3	2.3	2.2	2.6
Liters C_2H_4 produced per cu. meter butanes charged	39	46	52	..	..
Liters of C_3H_6 + C_4H_8 produced per cu. meter butanes charged	218	210	204	..	..
Liters butanes reacted per cu. meter butanes charged	512	445	417	298	388

Commercial Butane

Commercial butane (80 per cent *n*-butane and 20 per cent isobutane) was treated by the same method employed with propane. The decomposition or conversion per pass through the apparatus was about 40 per cent to prevent coke formation. A summary of the runs and conditions is given in Table III.

Table III also contains two experiments on butane combined feed. This combined feed is the material that would be continuously charged to the unit if the commercial butane were being processed with a recovery of 60 per cent condensable gas for recycling. This combined feed is then a mixture of 60 parts of recovered condensable gas plus 40 parts of fresh butane. By means of this operation only noncondensable gas and liquid products would be produced. In such an operation 1 cubic meter of the commercial butane would give 0.83 liter (6.2 gallons per 1000 cubic feet) of liquid product and 1.5 cubic meters of noncondensable gas with a molecular weight of 25.

It is also possible to operate the process so that the olefins are recovered at the end of each cycle and only butane is recycled. The calculated yields from 1 cubic meter of butanes by such a process would be as follows:

Run No.	3	4	5
Noncondensable gas, liters	1000	860	840 (olefin-free)
Ethylene, liters	76	103	112
$C_3H_6 + C_4H_8$, liters	367	400	404
Liquid:			
Liters	0.69	0.67	0.71
Gal./M cu. ft.	5.2	5.0	5.3

From these calculations it may be concluded that 1 cubic meter of butane will yield between 350 and 400 liters of propylene plus butylene together with 0.67 liter of liquid product. About 85 to 90 per cent of the liquid product boils in the gasoline range. This gasoline fraction has an octane rating of 77 and a blending octane value of 93 (25 per cent blend in fuel A of 50 octane number), C. F. R. motor method.

Although the results obtained by treating relatively pure hydrocarbons in this process are interesting theoretically, it is also desirable to test the utility of the process on a mixture of hydrocarbons which are available as a fraction of natural gas. Such a fraction of natural gas was made available for these tests by the Virginia Gasoline & Oil Company of Clendenin, W. Va. A summary of the data obtained is given in Table IV.

Still larger quantities of liquid products are formed from the natural gas fraction than were obtained from butane or propane, and the recovered condensable gas contains from 24 to 28 per cent propene plus butene. The results obtained by processing a gas having the same composition as the condensable gas (recycle stock) are also given in Table IV. Here again liquid products are produced and the olefin concentration in the condensable gas is 21 to 24 per cent.

Calculations from these results indicate that by operating under recycling conditions so that the condensable gas is combined with the appropriate quantity of fresh charge, 1 cubic meter of natural gas fraction would produce 1.63 cubic meters of noncondensable gas and 1.33 liters (10 gallons per 1000 cubic feet) of liquid product. In this type of operation no gaseous olefins would be removed from the condensable gas before recycling.

In operating to produce noncondensable gas, olefins, and liquid, removing the olefins between each cycle, and recycling only paraffins, it is estimated that 1 cubic meter of the Clendenin gas would give the following:

Substance	Yield
Noncondensable gas, liters	700 (olefin-free)
C_2H_4, liters	63
$C_3H_6 + C_4H_8$, liters	500
Liquid:	
Liters	1.0
Gal. per M cu. ft.	7.5

In making this calculation, due allowance has been given to the fact that the paraffins available for recycle have a lower average molecular weight (50) than the original charge (60).

Effect of Pressure

In all of the preceding experiments, the pressure was 51 kg. per square cm. (725 pounds per square inch). It is desirable to know whether this is the best operating pressure; therefore the pressure is varied while the other factors are kept constant. However, with a number of interrelated variables (pressure, temperature, contact time, and conversion per pass or per cent decomposed) controlling the final results, it is not possible experimentally to hold all these constant. For this reason there are two different methods of arriving at the effect of pressure. One is to hold temperature and contact time constant and vary the pressure. The other method is to hold the temperature and conversion per pass (per cent decomposition) constant while varying the pressure. For a first-order reaction the same contact time should give the same per cent decomposed at different pressures since the reaction rate is independent of concentration or pressure. In this case both methods would show the same effect of pressure. In the present study this was not true. As is shown in Table V, increasing the pressure increases the reaction rate (increases the conversion in unit time) and increases the liquid obtained from a given amount of reacted charge. Thus 86 seconds contact time at 70 kg. per square cm. (1000 pounds per square inch) gives the same percentage of charge decomposed (38.5 per cent) as

Table IV. Pyrolysis of Natural Gas Fraction at 51 Kg. per Square Cm. (725 Pounds per Square Inch) Pressure

	Natural Gas Fraction				Recycle Stock		
Run No.	8	9	10	11	12	13	14
Temp., ° C.	550	550	550	550	537	537	537
Contact time, sec.	123	107	86	67	80	83	86[a]
Gas charged, liters	860	710	892	1198	829	982	874
Products:							
Weight per cent of gas charged recovered as:							
Noncondensable gas	20.1	17.4	17.7	16.0	16.5	14.4	13.3
Condensable gas	61.6	67.2	70.7	72.8	64.5	64.2	68.3
Liquid product	19.2	16.0	13.2	10.1	15.5	14.7	15.2
Weight per cent of charge as unaccounted loss or gain	−0.9	−0.6	−1.6	1.1	3.5	6.7	3.2
Liters noncondensable gas produced	470	328	430	448	262	277	229
In noncondensable gas:							
Vol. per cent C_2H_4	5.2	2.3	3.1	4.1	5.3	2.8	2.1
Vol., per cent C_3H_6	3.2	4.6	7.5	7.6	4.3	9.3	8.9
Liters C_2H_4	19.2	7.6	13.3	18.4	13.9	7.6	4.8
Liters C_3H_6	15.0	15.0	32.3	34.0	11.3	25.7	20.4
Av. mol. weight noncondensable gas	22.1	22.7	22.0	25.5	28.0	27.4	27.0
Liters of condensable gas produced	643	567	730	996	564	689	640
In condensable gas:							
Vol. per cent C_2H_4	1.3	2.1	1.6	2.3	3.5	3.3	3.0
Vol. per cent $C_3H_6 + C_4H_8$	25.6	26.2	24.3	28.2	20.8	23.9	24.3
Liters C_2H_4	8.2	11.9	11.6	9.6	19.8	22.9	19.2
Liters $C_3H_6 + C_4H_8$	164	148	177	281	117	165	155
Av. mol. weight of condensable gas	49.7	50.5	52.0	52.3	51.0	51.0	49.0
Liquid:							
Liters per cu. meter gas charged	0.64	0.53	0.44	0.35	0.44	0.43	0.43
Gal. per M cu. ft. gas charged	4.8	4.0	3.3	2.6	3.3	3.2	3.2
Liters C_2H_4 per cu. meter gas charged	38	27	28	34	..	..	..
Liters $C_3H_6 + C_4H_8$ per cu. meter gas charged	208	229	234	267	..	..	..
Liters gas reacted per cu. meter gas charged	455	429	392	426[a]	213	217	194

[a] These values are not in agreement with other values in the table.

TABLE V. EFFECT OF PRESSURE ON THE PYROLYSIS OF NATURAL GAS FRACTION AT 550° C.

Run No.	15	16	17	18	19
Pressure, kg./sq. cm.	17.5	35	51	70	70
Contact time, sec.	133	127	121	123	86
Gas charged, liters	289	595	606	606	973
Products, weight per cent of gas charge:					
Recovered as noncondensable gas	32.1	21.2	28.1	30.5	25.7
Recovered as condensable gas:	61.5	67.2	55.7	51.0	61.2
Recovered as liquid product	6.4	10.3	17.0	19.2	16.3
As unaccounted loss	...	1.3	−0.8	−0.7	−3.2
Liters noncondensable gas produced	192	306	419	465	575
In noncondensable gas:					
Vol. per cent C_2H_4	4.3	3.1	2.7	1.4	1.6
Vol. per cent C_2H_6	13.1	8.3	7.2	5.7	8.4
Liters C_2H_4	8.2	9.3	11.3	6.5	9.1
Liters C_3H_6	25.2	25.5	30.0	26.6	48.1
Av. mol. weight noncondensable gas	28.9	24.6	24.4	23.6	26.0
Liters condensable gas produced	195	449	397	358	707
In condensable gas:					
Vol. per cent C_2H_4	2.6	2.9	2.2	1.8	2.9
Vol. per cent $C_3H_6 + C_4H_8$	24.2	23.8	27.4	25.0	21.7
Liters C_2H_4	5.1	13.0	8.8	6.5	20.9
Liters $C_3H_6 + C_4H_8$	47.2	107	108	89	154
Av. mol. weight condensable gas	54.5	53.0	51.0	51.3	50.3
Liquid:					
Liters per cu. meter of gas charged	0.19	0.33	0.52	0.59	0.52
Gal. per M cu. ft. gas charged	1.4	2.5	3.9	4.4	3.9
Liters C_2H_4 per cu. meter gas charged	46	38	33	21	30
Liters $C_3H_6 + C_4H_8$ per cu. meter gas charged	248	223	229	191	206
Liters gas reacted per cu. meter gas charged	501	445	539	570	452
K_1	0.313	0.278	0.383	0.412	0.418
K_2	1.80	0.748	0.783	0.643	0.571

was obtained with a contact time of 133 seconds at 17.5 kg. per square cm. (250 pounds per square inch). Also 38.5 per cent decomposition at 17.5 kg. per square cm. gives a liquid yield of 0.19 liter per cubic meter (1.4 gallons per 1000 cubic feet), while at 70 kg. per sq. cm. 38.8 per cent decomposition gives 0.52 liter per cubic meter (3.9 gallons per 1000 cubic feet).

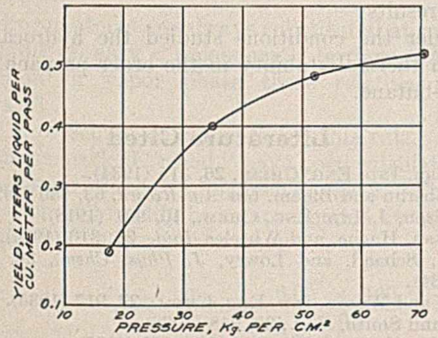

FIGURE 2. RELATION BETWEEN YIELD AND PRESSURE

Temperature, 550° C.; 40 per cent of charge reacted.

Since a given percentage decomposition or conversion gives a lower liquid yield at 17.5 kg. per square cm., it is to be expected that the yield of olefins would be correspondingly higher at the lower pressure. Table V shows that the olefin yield is higher at 17.5 than at 70 kg. per square cm., confirming the close relationship between olefin yield and liquid yield.

From the practical point of view it is interesting to find the effect of pressure on the yield of liquid products. From the data in Table V estimates of the liquid yield at constant conversion (40 per cent conversion, 60 per cent recovery of condensable gas) have been made. These results are plotted in Figure 2 which shows that the operating pressure should be between 51 and 70 kg. per square cm. for optimum liquid production. Although actual experiments have not been made, the indication is that the effect of pressure on the liquid yield from a given amount of charge reacted becomes asymptotic above 70 kg. per square cm. For this particular gas the pressure used, 51 kg. per square cm., is sufficient, and since this gas acts very much like the commercial butanes it is assumed that the pressure is adequate in that case also.

Relation between Average Molecular Weight of Gas Charged and Ultimate Liquid Yield

As a result of the studies with the paraffin gases, sufficient data have been obtained to indicate just what ultimate liquid yields may be expected from a given gas when processed by recycling in this apparatus under the conditions of temperature and pressure employed. Figure 3 indicates the liquid yields in liters per cubic meter and in weight per cent of the charge, which can be obtained by processing a gas of a known average molecular weight. In the experiments which have been made, the curves apply to mixtures as well as to relatively pure compounds with the exception of isobutane or gases rich in isobutane. The yields given are for recycle operation in which only liquid and noncondensable gas are produced.

The data can also be used to calculate the yields of olefins and liquids available if the olefins are removed from the gases and only the paraffins recycled. The following tabulation summarizes such calculations:

Hydrocarbon Charged	Liters of Products from 1 Cu. Meter of Charge			
	$CH_4 + C_2H_6$	C_2H_4	$C_3H_6 + C_4H_8$	Liquid
Propane	950	98	123	0.20
Butane	850	100	400	0.67
Natural gas fraction	700	63	500	1.00

Properties and Uses for Products

The experiments indicate that the yield of noncondensable gas formed varies between 800 and 1500 liters for every cubic meter of gas reacted, depending on the gas charged and the operating conditions. This gas was practically pure methane and ethane.

The propene plus butenes produced may be polymerized catalytically to gasoline (*9*, *10*). By using such a process to polymerize quantitatively these olefins between cycles, it is estimated that the olefins from the commercial butane will yield an additional 0.87 liter of liquid per cubic meter (6.5 gallons per 1000 cubic feet) of gas reacted or a total of 1.54 liters per cubic meter (11.5 gallons per 1000 cubic feet). Similarly with the natural gas fraction, the olefins should yield

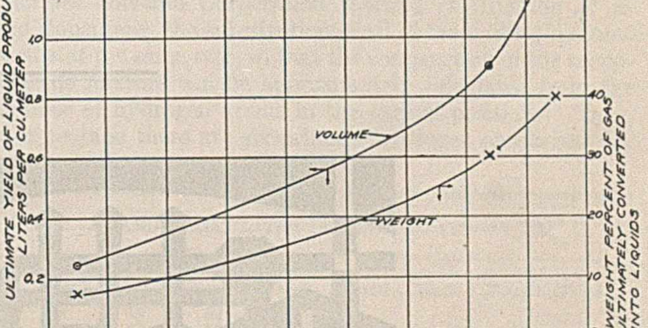

FIGURE 3. RELATION BETWEEN ULTIMATE YIELD OF LIQUID PRODUCTS AND MOLECULAR WEIGHT OF GAS CHARGED

TABLE VI. PROPERTIES OF LIQUID PRODUCTS FROM CLENDENIN, W. VA., NATURAL GAS FRACTION

Run No.	Original Natural Gas Fraction 8	9	10	11	Clendenin Recycle Blend 12 + 13 + 14
Density of crude fraction, 15° C.	0.723	0.721	0.723	0.701	0.752
A. P. I. gr. of crude fraction, 15° C.	64.1	64.7	64.3	68.7	56.7
100-cc. Engler distillation, ° C.:					
Initial boiling point	29	29	29	33	36
10 per cent over	34	35	37	41	44
20 per cent over	42	40	48	45	53
50 per cent over	64	68	69	62	90
90 per cent over	219	237	194	181	251
End point	306	253	281	271	265
End-point (225° C.) gasoline, per cent	90.5	89.5	91.5	93.0	88.0
Density of gasoline, 15° C.	0.722	0.707	0.706	0.699	0.731
A. P. I. gr. of gasoline, 15° C.	64.6	68.5	68.9	70.9	62.1
Octane No. of gasoline	77	...	77	76	...
Blending octane No. of gasoline[a]	93	93	93	89	93

[a] The blending octane number was made by mixing 25 per cent of the liquid to be tested with 75 per cent fuel A which had an octane number of 50. The octane numbers were determined by the C. F. R. motor method.

an additional 1.07 liters (8 gallons) of liquid or a total of 2.07 liters per cubic meter (15.5 gallons per 1000 cubic feet) of gas reacted. The gasoline produced by the catalytic polymerization has a somewhat higher octane rating and blending value than the gasoline produced by pressure pyrolysis of the butanes.

The calculated yields of products from 1 cubic meter of gas treated by pressure pyrolysis combined with catalytic polymerization of the propene plus butene are given in the following table:

Hydrocarbon Charged	Liters of Products from 1 Cu. Meter of Charge $CH_4 + C_2H_6$	C_2H_4	Liquid
Propane	950	98	0.53
Butane	850	100	1.54
Natural gas fraction	700	63	2.07

Since it was proposed to use the liquid products produced by the present pyrolytic process as motor fuel, it was desirable to study a few of the properties of the liquids that are characteristic of motor fuels. The crude liquids generally had a yellow color and gasoline distilled from the crude liquid was colorless or had a slight yellow color. The odor of both the crude and the gasoline was suggestive of that of styrene or indene. The fractions above gasoline were similar to highly cracked petroleum products.

Table VI gives a summary of the properties of the liquids.

Summary and Conclusions

1. Propane was pyrolyzed under 51 kg. per square cm. (725 pounds per square inch) at 550° and 575° C. By recycling the unreacted gas it is estimated that 1 cubic meter of propane will yield 950 liters of methane plus ethane, 98 liters of ethylene, 123 liters of propene, and 0.2 liter of liquid. By catalytically polymerizing the propene to liquid, it is estimated that the liquid yield will be increased to 0.53 liter per cubic meter (4 gallons per 1000 cubic feet).

2. Commercial butane was pyrolyzed at 51 kg. per square cm. (725 pounds per square inch) and 550° C. It is estimated that 1 cubic meter of butane will yield, with recycle operation, 850 liters of methane plus ethane, 100 liters of ethylene, 400 liters of propene plus butenes, and 0.67 liter of liquid product. Catalytic polymerization of the propene plus butenes will increase the liquid yield to 1.54 liters (11.5 gallons per 1000 cubic feet).

3. A natural gas fraction containing 2.5 per cent "air plus methane," 5.7 per cent propane, 50.5 per cent *n*-butane, 13.0 per cent isobutane, and 28.3 per cent pentanes, was pyrolyzed at 550° C. and at pressures from 17.5 to 70 kg. per square cm. (250 to 1000 pounds per square inch). At 51 kg. per square cm. (725 pounds per square inch) under recycling conditions it is estimated that 1 cubic meter of the natural gas fraction will yield 700 liters of methane plus ethane, 63 liters of ethylene, 500 liters of propene plus butenes, and 1.0 liter of liquid product. An additional 1.07 liters of liquid may be obtained by catalytically polymerizing the propene plus butenes, bringing the total liquid yield to 2.07 liters (15.5 gallons per 1000 cubic feet).

4. It was found as the pressure was increased from 17.5 to 70 kg. per square cm. (250 to 1000 pounds per square inch), other conditions being unchanged, that the liquid yield increased at the expense of the olefin yield.

5. The liquid produced by the pressure pyrolysis had an octane number of 77 when run straight, or 93 in a 25 per cent blend with fuel A of 50 octane number (C.F.R. motor method).

6. Reactions are proposed which seem to account for the observed results.

7. Under the conditions studied the hydrocarbons decreased in thermal stability in the order propane > isobutane > *n*-butane.

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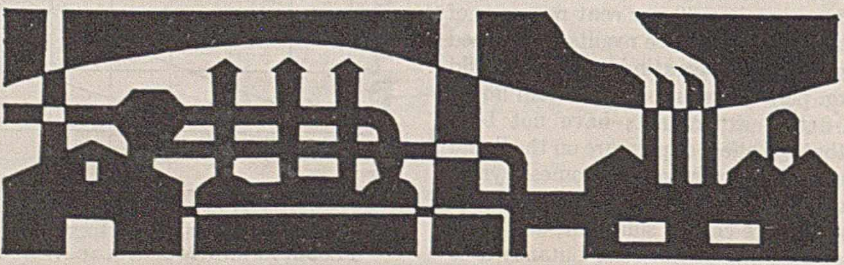

Chlorination of Paraffins[1]

Factors Affecting Yields of Isomeric Monochlorides and Dichlorides

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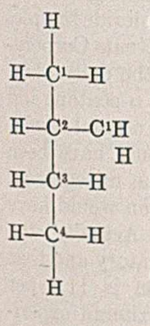
A method is given for calculating from the structural formula of any paraffin hydrocarbon the percentages of its various isomeric monochlorides obtainable by noncatalytic chlorination at temperatures from −65° to +600° C. The effects upon the isomeric ratios of temperature, liquid-phase reaction, vapor-phase reaction, light, carbon surfaces, reaction rate, excess of hydrocarbon, and structure of hydrocarbon were studied. Methods were not evolved for the quantitative prediction of the proportions of isomeric dichlorides obtained, but in vapor-phase chlorination there is a tendency which minimizes the yields of dihalides containing two chlorine atoms on the same carbon atom. Herzfelder's rule to the effect that the only dihalides formed are those containing halogen atoms attached to adjacent carbon atoms does not apply to chlorinations where all isomers derivable without carbon skeleton rearrangement are always formed.

A DISCUSSION of the somewhat scanty and often inaccurate literature in the field of the chlorination of the simpler paraffins is contained in a previous paper of this series (*4*). The same article describes the type of chlorination apparatus most frequently used here, the methods of analysis of the chloride mixtures obtained, and the evidence for rule 1. The results reported in the present article were obtained in the same manner except where specific details were changed and are so reported. The methods of analysis of the monochloride mixtures derived from *n*-pentane and isopentane are covered in a separate article (*5*).

Chlorination Rule 2

The hydrogen atoms are always substituted at rates which are in the order primary < secondary < tertiary. At 300° C. with reaction in vapor phase these relative rates are 1.00:3.25:4.43.

Table I is presented as evidence for this rule. The data in the columns marked "calcd." have been calculated on the basis of the empirical constants given in rule 2. The method of computation will readily be comprehended by using a specific example, in this case isopentane:



$$6 \times 1.00 = 6.00; \quad \frac{6.00 \times 100}{19.93} = 30.1\%$$

1-chloro-2-methylbutane

$$1 \times 4.43 = 4.43; \quad \frac{4.43 \times 100}{19.93} = 22.2\%$$

2-chloro-2-methylbutane

$$2 \times 3.25 = 6.50; \quad \frac{6.50 \times 100}{19.93} = 32.6\%$$

3-chloro-2-methylbutane

$$3 \times 1.00 = \frac{3.00}{19.93}; \quad \frac{3.00 \times 100}{19.93} = 15.1\%$$

4-chloro-2-methylbutane

There are six hydrogen atoms attached to carbon atoms in the positions numbered 1 in the formula. These are primary hydrogen atoms, and under the conditions their relative reaction rate is 1.00. The product of the number of hydrogen atoms in this position multiplied by the relative reaction rate gives the chance of the chlorine substituting in this position to yield 1-chloro-2-methylbutane. The sum of all such products for isopentane under these conditions is 19.93, so (6 × 100/19.93) gives the percentage of 1-chloro-2-methylbutane in the monochlorides. A reversal of this calculation enables us to obtain the relative reaction rates from the composition of the monochloride mixtures. It is understood in applying the rule that conditions must be selected so that pyrolysis is substantially eliminated and only a very small amount of monochloride is carried to a higher state of chlorination. The experimental data in Table I were obtained before the method of calculation was worked out.

Agreement is excellent except in the case of isopentane where it is only fair, but the analysis of the mixture of the four monochlorides derived from isopentane is more difficult and less precise than for the other monochloride mixtures.

The only serious contradiction to rule 2 in the literature, other than the fragmentary research of Schorlemmer (*10*), performed two-thirds of a century ago, in which he failed to detect the presence of 2-chloropropane at all, is the one made by Ayres (*1*) and repeated by Clark (*2*); that is, in the Sharples Solvents Corporation thermal chlorination of *n*- and isopentane, the substitution of all of the hydrogen atoms occurs at the same rate, so that the composition of the monochloride mixture can be approximately calculated from the number of hydrogen atoms in the various positions. Thus, in *n*-pentane there are six primary hydrogen atoms and six

TABLE I. OBSERVED AND CALCULATED ISOMERIC RATIOS AT 300° C.

	Isomeric Monochloride, Per Cent							
	1-Chloro		2-Chloro		3-Chloro		4-Chloro	
Hydrocarbon	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Propane	48	48	52	52	..	..	..	..
2-Methylpropane	67	67	33	33	..	..	..	..
Butane	32	32	68	68	..	..	..	..
2-Methylbutane	33.5	30	22	22	28	33	16.5	15
n-Pentane	23.8	23.5	48.8	51	27.4	25.5	..	..

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[1] This paper is the third in a series on the subject of syntheses from natural gas hydrocarbons. The first two articles appeared in IND. ENG. CHEM., 23, 352 (1931) and 27, 1190 (1935).

TABLE II. EFFECT OF TEMPERATURE UPON RELATIVE CHLORINATION RATES OF PRIMARY, SECONDARY, AND TERTIARY HYDROGEN ATOMS IN VAPOR PHASE

Expt. No.	Hydrocarbon	Temp.	Light or Dark	Ratio, HC: Cl_2	Equivalent of: HCl formed	Equivalent of: Organic Cl_2 recovered	Ratio, Monochlorides: Polychlorides	Primary	Secondary	Tertiary	Relative Activity of H Atom: Secondary: primary	Relative Activity of H Atom: Tertiary: primary	Mixing Temp.	Total Vol. Monochlorides	Polychlorides by Vol.
		° C.		*Moles*			*Grams*	%	%	%			° C.	*Ml.*	%
1 B	Propane	490	D	2	..	2.06	5.77	55.7	44.3	..	2.35	..	30	149	11.3
2 B	Propane	300	D	2	..	2.11	4.74	47.6	52.4	..	3.2	..	30	145	14.7
4 B	Propane	600	D	9	..	1.61	20.8	57.8	42.2	..	2.19	..	600	135	3.5
5 B	Propane	475	D	21	..	1.61	20.0	53.9	46.1	..	2.56	..	475	130	3.7
6 B	Propane	550	D	16	..	1.5	11.6	58.4	41.6	..	2.14	..	550	120	6.6
169	Propane	80	L	3.3	..	0.95	3.12	40.7	59.3	..	4.36	..	30	59	23.0
172	Propane	80	L	2.8	..	0.72	7.3	38.5	61.5	..	4.7	..	30	57	6.8
8	Propane	300	D	8	..	2.19	13.6	47.2	52.8	..	3.35	..	30	178	5.3
1	Propane	50	L	3	..	5.12	4.07	40.0	60.0	..	4.45	..	30	235	9.0
3	Propane	65	L	1	..	4.6	1.97	38.8	61.2	..	4.73	..	30	155	30.2
157	Isobutane	80	L	2	..	0.8	4.26	57.5	..	42.5	..	6.66	30	54	16.6
160	Isobutane	80	L	2.1	..	1.31	3.28	54.7	..	45.3	..	7.45	30	76	19.1
161	Isobutane	80	L	2	..	1.99	4.65	54.8	..	45.2	..	7.4	30	137	14.4
146	Isobutane	335	L	4.6	2.4	2.06	9.2	65.0	..	35.0	..	4.84	350	177	8.4
1 C	Isobutane	400	D	2	1.98	1.71	5.4	70.8	..	29.2	..	3.71	400	144	12.7
3 C	Isobutane	325	D	2	1.74	1.53	3.32	68.8	..	31.2	..	4.23	325	114	19.1
4 C	Isobutane	375	D	2	1.79	1.51	5.45	69.1	..	30.9	..	4.03	375	126	13.7
5 C	Isobutane	400	D	8	..	1.32	10.8	70.2	..	29.8	..	3.83	400	124	6.7
6 C	Isobutane	600	D	2	2.96	1.52	6.55	76.5	..	23.5	..	2.76	600	132	10.8
3 D	Isobutane	300	D	2	4.13	3.67	4.59	66.5	..	33.5	..	4.54	30	298	14.6
4 D	Isobutane	300	D	2	4.28	3.71	4.54	66.7	..	33.3	..	4.49	30	300	14.7
10 D	Isobutane	300	D	2	3.97	3.47	4.89	66.8	..	33.2	..	4.47	30	286	13.8
1 D	Isobutane	300	D	5	3.49	3.21	12.0	67.3	..	32.7	..	4.38	30	305	6.2
2 D	Isobutane	300	D	5	3.48	3.21	12.0	67.3	..	32.7	..	4.38	30	305	6.2
6 D	Isobutane	300	D	5	3.14	3.03	11.7	66.6	..	33.4	..	4.52	30	294	6.2
5 D	Isobutane	300	D	8	3.7	3.44	17.8	67.6	..	32.4	..	4.33	30	340	4.2
9 D	Isobutane	300	D	8	3.71	3.38	17.5	67.0	..	32.3	..	4.34	30	333	4.3
22	Butane	300	D	7	2.933	3.048	5.9	32.0	68.0	..	3.19	..	300	262.6	8.33
10 W	Pentene	330	D	16	0.68	0.66	12.4	24.0	76.0	..	3.2	..	330	70.8	6.0
11 W	Isopentane	330	D	16	0.76	0.72	12.3	50.0	28.0	22.0	2.5	4.0	330	73	6.0
12 W	Pentane	400	D	7.5	1.8	1.1	8.4	30.0	70.0	..	2.3	..	400	115	8.7

secondary hydrogen atoms, and we would therefore expect (assuming a nonselective chlorination) 50 per cent primary and 50 per cent secondary isomers. The value reported by Ayres is 48 per cent primary and 52 per cent secondary chlorides, a very good agreement. However, neither Ayres nor Clark attempted an analysis of the monochlorides of the pentanes until after they had first been converted to alcohols by action of sodium oleate, water, and sodium hydroxide. This conversion involves prolonged heating under pressure at about 170° C., recycling, and continuous operation, conditions which are not readily duplicated in the laboratory and whose effect upon the isomeric ratios is difficult to evaluate.

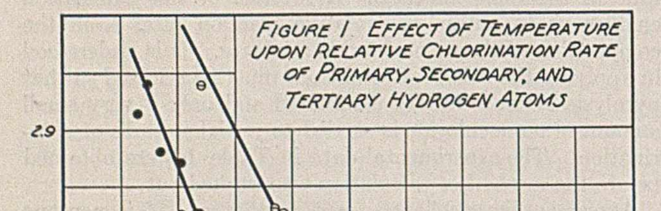
FIGURE I. EFFECT OF TEMPERATURE UPON RELATIVE CHLORINATION RATE OF PRIMARY, SECONDARY, AND TERTIARY HYDROGEN ATOMS

After the isomeric amyl chlorides had all been synthesized in a pure form and their boiling points redetermined in this laboratory, it became apparent that 1-chloropentane boils at least 8° C. higher than any of its isomers. With modern laboratory rectification equipment it is relatively simple to separate 1-chloropentane from the other amyl chlorides almost quantitatively and to estimate its concentration in the original mixture. Simultaneously, a similar analysis was made of the mixture of *n*- and isopentane used as starting material for the chlorination. The pentane and amyl chloride samples were both kindly furnished by the Sharples Solvents Corporation and were stated to be representative of the daily plant operation. The pentanes analyzed 53 per cent *n*-pentane and 47 per cent isopentane. If 48 per cent of the normal isomer were converted to 1-chloropentane, there would have been about 25.4 per cent of 1-chloropentane in the mixed amyl chlorides. A perfectly nonselective chlorination would have resulted in 26.5 per cent 1-chloropentane. Actually, the average of the analysis performed in this laboratory and that by Olin of the Sharples Solvent Corporation is 11.8 per cent. This difference is many times the maximum experimental error and demonstrates that nonselective chlorination is not obtained under Sharples conditions. The writers believe that the relatively high proportion of primary alcohols reported present in Pentasol is due not to a nonselective chlorination but to a selective destruction of the secondary and tertiary chlorides in the steel chlorinator and in the digesters.

The same considerations apply to the statement (*1*, *2*) that more 3-chloropentane than 2-chloropentane is obtained in the thermal chlorination of pentane. This means that more 3-pentanol than 2-pentanol is found in Pentasol. There is much evidence (*11*) that the "positive fragments," as Whitmore (*13*) would call them, $C_5{}^+H_{11}$, of either of the secondary halides of *n*-pentane isomerize readily to an equilibrium mixture of both, so that any analyses performed after conversion of these chlorides to alcohols at 170° C. gives very little information as to the isomeric ratios originally present. Analyses following the technic which Lauer and Stodola (7) worked out for the corresponding bromides show that the quantity of 2-chloropentane formed on chlorinating *n*-pentane is, within the limits of accuracy of the analytical method, exactly twice as great as the amount of 3-chloropentane. This is in agreement with rule 2, since there are twice as many hydrogen atoms in the 2 as in the 3 position and all hydrogens in the 2 and 3 positions of *n*-pentane are secondary.

Chlorination Rule 3

At increasing temperatures there is increasingly close approach to relative rates of 1:1:1 in both liquid and vapor phase.

Evidence for this generalization is given in Figures 1 and 2 and Tables II and III; the relative rates of secondary and tertiary hydrogen atoms are shown to vary with temperature in both vapor and liquid phases. The relative substitution rate of a primary hydrogen atom is taken as 1.

By the use of these graphs one can find the relative reaction rates which may be used as shown to obtain the isomeric ratios. We can thus estimate from the structural formula of any paraffin hydrocarbon the relative proportions of the various isomeric monochlorides which can be obtained by chlorination under any of the conditions covered by the graph.

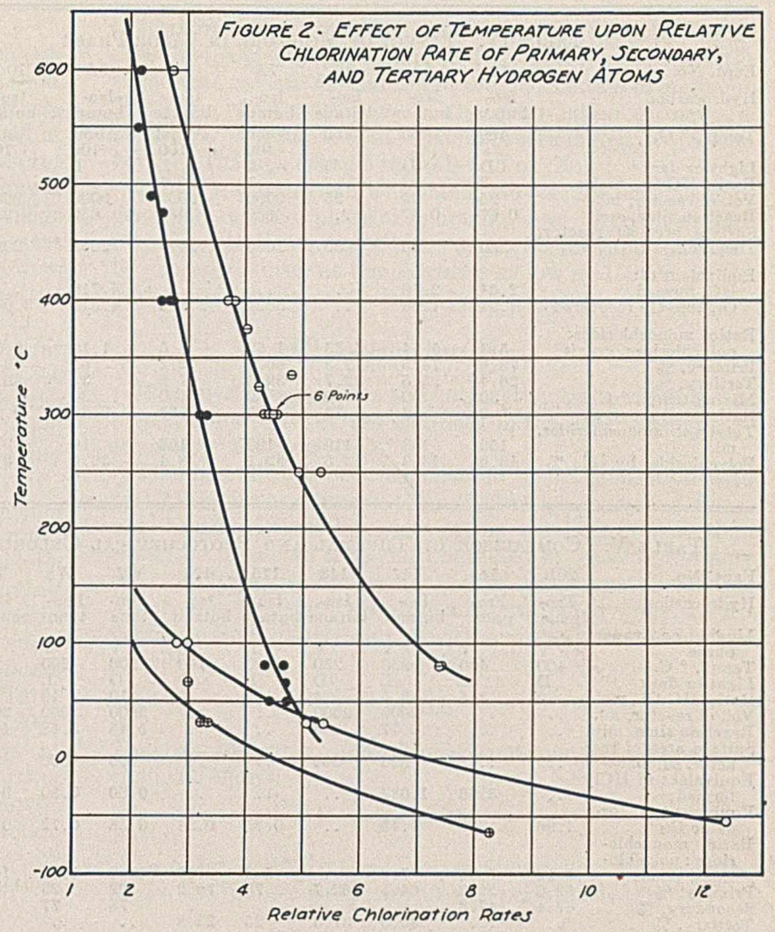
FIGURE 2. EFFECT OF TEMPERATURE UPON RELATIVE CHLORINATION RATE OF PRIMARY, SECONDARY, AND TERTIARY HYDROGEN ATOMS

Certain precautions must be observed in applying these curves. The different monochlorides may chlorinate to dichlorides, trichlorides, etc., at different rates. This would change their ratios in the monochloride fraction so that results are most accurate when not more than a small proportion of monochloride is converted to dichloride. This is the condition always used in commercial operation for obtaining monochlorides, for reasons of economy. At low temperatures, where substantially no olefin formation occurs, results are not complicated by selective pyrolysis, but when operating at temperatures above 300° C. we can easily get the impression that a nonselective chlorination is taking place, whereas actually the tertiary and/or secondary chlorides are being preferentially decomposed. When pyrolysis becomes appreciable, (1) the organic chlorine fails to balance the chlorine present as hydrochloric acid, (2) olefins appear in the recovered hydrocarbon, and (3) especially if recycling is used, chloroölefins appear in the organic chloride fractions. In an experiment (Table VI) with isobutane using a small steel tube as chlorinator at 450° C. without recycling, the yield of isobutyl chloride amounted to 99 per cent of the monochloride fraction. This might indicate that iron is a catalyst favoring primary substitution, were it not that excess hydrochloric acid and olefin formation indicate that the usual percentage of tertiary chloride had been formed and subsequently decomposed. Iron is a pyrolysis catalyst for chloroparaffins, and the results on which Figure 1 is based were therefore obtained in glass apparatus. Similar results were obtained with propane, *n*-butane, and the pentanes. Metals such as monel, nickel, or KA2 alloy may be used without increasing pyrolysis unduly. At high temperatures, even in glass apparatus, yields of primary chlorides may equal or exceed those calculated on the basis of nonselective chlorination, but always with the accompaniment of excess hydrochloric acid and olefin formation sufficient to account for the results.

Still another precaution is mentioned in the second article of this series (4) under "Temperature Control." If chlorine and hydrocarbon vapor are mixed and subsequently heated to reaction temperature, chlorination inevitably occurs at all temperatures from about 250° C. (at which reaction be-

TABLE III. EFFECT OF TEMPERATURE UPON RELATIVE CHLORINATION RATES OF PRIMARY, SECONDARY, AND TERTIARY HYDROGEN ATOMS IN LIQUID PHASE

Expt. No.	150	164	{162 170}	178	152	163	175	176	28	174
Hydrocarbon	Propane	Propane	Propane	Propane	Isobutane	Isobutane	Isobutane	Iso butane	Isobutane	Pentane
Ratio, HC:Cl_2, moles	..	2	..	2.3	..	2	2	2	...	..
Temp., ° C.	−60	30	30	75(?)	30	30	100	100	−55	−60
Light or dark	L	L	L	L	L	L	L	D	L	L
Ratio, monochlorides:polychlorides, grams	3.9	8.4	15.7	4.75	26.6	..	5.14	3.6	5.95	..
Primary, %	26.6	48.2	47	50	62.5	64	75	76.2	42	9
Secondary, %	73.4	51.8	53	50	..	..	..	..	...	91
Tertiary, %	..	..	..	...	37.5	36	25	23.8	58	..
Relative activity of H atoms:										
Secondary:primary	8.3	3.22	5.8	3.0	..	..	..	..	...	10.1
Tertiary:primary	..	..	..	...	5.4	5.08	3.0	2.81	12.4	..
Mixing temp., ° C.	−60	Liquid air	Liquid air	Liquid air	Liquid air	Liquid air	Liquid air	Liquid air	Liquid air	−60
Total vol. monochlorides, ml.	211	22	41	32	28	26	30	18.4	283	14.2
Polychlorides by vol., per cent	16	8.3	4.5	14	24.3	..	13	18	11.65	..

comes rapid enough to affect the results) to the highest temperature attained. This was avoided in the present work, when the effect of temperature was being investigated above 250° C., by preheating both chlorine and hydrocarbon to reaction temperature and then mixing at an extremely rapid rate (flow of chlorine, about 50 miles per minute) under conditions of very close temperature control.

Chlorination Rule 4

Liquid-phase chlorination gives relative rates of primary, secondary, and tertiary substitution which are obtainable only at much higher temperature in vapor phase. This is obvious from an inspection of Figures 1 and 2 and Tables II and III.

A given temperature change produces a much greater difference in relative reaction rates of primary, secondary, and tertiary hydrogens when one is operating in liquid phase than when the chlorination takes place in gaseous phase. This means that the isomeric ratios are much more readily controllable in liquid than in vapor phase. Maximum yields of either primary isomers (at high temperatures) or secondary or tertiary isomers (at low temperatures) can be obtained by operating with the reagents in liquid form. In case the critical temperature of the hydrocarbon is inconveniently low, the chlorination may be carried out using carbon tetrachloride as a solvent (Table VII) without affecting the ratios of isomers. Obviously a considerable pressure develops at the higher temperatures, because of hydrogen chloride formation, even when this diluent is used. Apparently, then, the pronounced difference in the slopes of the curves obtained in liquid phase and in vapor phase indicates a difference in reaction mechanism. This subject will be further investigated.[2]

Chlorination Rule 5

The presence or absence of the following factors does not affect appreciably the relative rates of primary, secondary, and tertiary substitution: (*a*) moisture, (*b*) carbon surfaces, (*c*) light.

EFFECT OF MOISTURE. In experiment 4A (Table IV) the isobutane and chlorine were dried by passing them separately through sulfuric acid wash bottles and then through sulfuric acid absorption towers with sintered glass bottoms. Glass beads were placed in the towers so that the fine bubbles, produced by passage of the gases through the sintered glass, would be repeatedly distorted in their passage up the tube.

TABLE IV. EFFECT OF MOISTURE IN VAPOR PHASE

Expt. No.	4A	5A	6A	7A	8A	9A	10A	11A
Hydrocarbon	Isobutane	Isobutane	Isobutane	Isobutane	Isobutane	Isobutane	Isobutane	Isobutane
Temp., ° C.	450	450	450	About 100	About 100	About 100	About 100	About 100
Light or dark	D	D	D	L	L	L	L	L
Ratio, HC:Cl_2, moles	3	3	..	1	5	1	5	5
Vol. of reactor, ml.	25	25	25	9000	9000	9000	9000	9000
Reaction time, sec.	0.67	0.67	..	650	434	650	288	288
Surface area of reactor, sq. cm.	50	50	50	2095	2095	2095	2095	2095
Equivalent of:								
HCl formed	2.54	2.18	..	..	...	4.719	...	..
Organic Cl_2 recovered	1.94	1.66	..	3.24	2.145	4.517	3.004	1.40
Ratio, monochlorides: polychlorides, grams	5.3	5.14	5.53	1.57	8.5	1.18	9.05	7
Primary, %	73.6	74.5	77.3	60.6	62.2	63	63.3	61.6
Tertiary, %	26.4	25.5	22.7	39.4	37.8	37	36.7	38.4
Mixing temp., ° C.	30	30	30	30	30	30	30	30
Ratio, wall area:vol.	2	2	2	0.23	0.23	0.23	0.23	0.23
Total vol. monochlorides, ml.	159	143	119	190	196	216	272	130
Polychlorides by vol., %	13.6	13.3	12.5	32.1	8.4	39.4	8.1	9.7

TABLE V. COMPARISON OF THERMAL AND PHOTOCHEMICAL CHLORINATION

Expt. No.	20B	145	147	148	175	176	W7	W8	W9	W10
Hydrocarbon	Propane	Propane	Isobutane	Isobutane	Isobutane	Isobutane	Pentane	Pentane	Isopentane	Isopentane
Liquid or vapor phase	V	V	V	V	L	L	V	V	V	V
Temp., ° C.	400	400	250	250	100	100	200	200	200	200
Light or dark	D	L	L	D	L	D	D	L	D	L
Ratio, HC:Cl_2, moles	2	3.5	3.5	4	2	2	10	10	12	8
Vol. of reactor, ml.	..	...	2000	2000	..	..	2000	2000	2000	2000
Reaction time, min.	..	...	0.77	2.8	..	..	5.48	5.48	4.62	6.67
Surface area of reactor, sq. cm.	..	...	800	800	..	..	800	800	800	800
Equivalent of HCl formed	..	3.66	1.637	..	..	..	0.60	0.80	0.52	0.62
Equivalent of organic Cl_2	1.96	2.3	1.45	..	0.36	0.24	0.58	0.72	0.53	0.55
Ratio, monochlorides : polychlorides, grams	3.92	7.06	7.8	..	5.2	3.62	12.0	11.9	14.2	16.4
Primary, %	52.6	52.2	64.5	62.7	75	76.2	22	23	48	47
Secondary, %	47.4	47.8	...	..	..	..	78	77	29	29
Tertiary, %	..	...	35.5	37.3	25	23.8	..	..	23	24
Relative activity of H atom:										
Secondary:primary	2.7	2.72	...	..	..	..	3.5	3.4	2.7	2.8
Tertiary:primary	..	...	4.95	5.35	3	2.81	..	..	4.3	4.6
Mixing temp., ° C.	400	400	250	250	Liquid air	Liquid air	200	200	200	200
Total vol. monochlorides, ml.	118	175.3	131	131	30	18.4	62.9	77.7	58.3	61.7
Polychlorides by vol., %	16.3	19	9	..	13	18	..	..	..	..

TABLE VI. EFFECT OF STEEL CHLORINATOR ON PYROLYSIS (ISOBUTANE IN VAPOR PHASE, DARK)

	Small Pyrex Reactor		Small Steel Reactor		Large Steel Reactor		Large Pyrex Reactor	
Expt. No.	5	29	6	10	8	9	16	17
Temp., ° C.	600	600	455	450	275	265	320	350
Ratio, HC : Cl_2, moles	7	9.2	7.6	7.4	8	9	10	11
Vol. of reactor, ml.	5.09	...	4.4	4.4	4170	4170	1650	1650
Reaction time, sec.	0.013	...	0.012	0.012	16	15	5.5	5.2
Surface area of reactor, sq. cm.	67	...	87.8	87.8	2200	2200	670	670
Equivalent of:								
HCl recovered	4.185	3.228	4.111	3.88	5.189	4.84	2.854	3.695
Organic Cl_2	2.897	1.915	2.43	2.68	3.1	3.34	2.15	2.85
Primary, %	86.9	82.2	100	97.8	100	100	83.5	77.1
Tertiary, %	13.1	17.8	0	2.2	0	0	16.5	22.9
Mixing temp., ° C.	600	600	455	450	100	100	200	500
Total vol. monochlorides, ml.	305	211	212	254	180	193	181	166
Polychlorides by vol., %	4.46	7.6	9.82	8.86	27.1	21.7	12.2	5.94

TABLE VII. CARBON TETRACHLORIDE AS DILUENT FOR LIQUID-PHASE CHLORINATION

Expt. No.	202	203
Hydrocarbon	Pentane	Pentane
Temp., ° C.	About 125	About 125
Light or dark	L	L
Ratio:		
HC:Cl_2, moles	4	4
HC:CCl_4, moles	∞	2
Monochlorides:polychlorides, grams	6.2	3.5
Primary, %	28.2	28.2
Secondary, %	71.8	71.8

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[2] The novel chlorination processes presented in this series are covered by U. S. Patents 2,004,072 and 2,004,073 (June 4, 1935) and others pending, all assigned to the Purdue Research Foundation.

There was no drying in experiment 5A.

In experiment 6A the isobutane was passed through a sulfuric acid wash bottle, a phosphorus pentoxide drying tube, and finally through a tube of molten sodium to remove traces of oxygen which might have formed moisture in the reactor. The chlorine was passed through sulfuric acid, phosphorus pentoxide, and activated coconut charcoal heated to redness. The charcoal converted any free oxygen to carbon monoxide and carbon dioxide. Before the experiment the apparatus was dried for several hours by a flame while the gases were passing through. All-glass connections were used from the phosphorus pentoxide tube through the reactor.

The effect of added moisture was also negative in so far as the isomeric ratios are concerned. In experiments 7A and 8A the isobutane was chlorinated just as it came from the reactor. In 9A and 10A the isobutane was bubbled through water, and in 11A steam was blown into the reaction chamber throughout the experiment.

EFFECT OF CARBON SURFACE. A number of experiments were performed in which the reactor was filled with granular coke, previously extracted for several weeks with hydrochloric acid. In another experiment the reactor was filled with glass wool, which soon became coated with a carbonaceous deposit. The isomeric ratios were unaffected.

EFFECT OF LIGHT. Evidence that the isomeric ratios are unaffected by the presence or absence of light is given in Table V. Probably the most significant results are those at 200° and 250° C. Vapor-phase thermal chlorination is slow at these temperatures so that when light was present most of the chlorination was caused by the absorption of photons.

These results would seem to indicate that the reaction mechanism is the same whether the chains are initiated by some catalytic effect at the carbon surfaces, by the reaction,

$$Cl_2 + h\nu \rightarrow 2Cl$$

or by simple thermal dissociation of chlorine molecules, and that water does not play any essential role in the system.

A reaction mechanism which is consistent with all of the writers' results is the following:

$$Cl_2 \rightarrow 2Cl$$
$$RH + Cl \rightarrow R— + HCl$$
$$R + Cl_2 \rightarrow RCl + Cl$$

In thermal chlorination the chlorine atoms are produced mainly by some wall reaction, presumably a catalytic chlorination on the surface of the carbonaceous deposit which soon forms on the glass walls of the reactor. The importance of this deposit is shown by the fact that, when the experiment is conducted in a clean glass reactor, there is a marked induction period during which chlorination is apt to be incomplete. If the walls are kept sufficiently cool, reaction is effectively inhibited, as shown by the following experiment:

> A 3-liter flask was equipped with a preheater for the reactants (chlorine and isobutane) and with an exit tube sealed to the bottom, opposite the inlet tubes. The flask was immersed in water and light was excluded. The chlorine and isobutane were separately preheated to 550° C. and mixed by forcing the chlorine from a jet at high velocity. There was no reaction. This result was explicable by the sudden cooling of the chlorine, issuing from the jet, by admixture with the gases in the flask; the temperature just below the mixing point had dropped to 100° C. When a 50-ml. flask was used in place of the larger one and it was immersed in boiling water, the temperature in the flask registered 325° C. at a point below the center. There was still no reaction. The same result was obtained when a 12-mm. tube was substituted for the flask.

In photochemical chlorination the chlorine molecules are decomposed by absorbing a quantum of blue light and the reaction chains are thus initiated. Deanesly (*3*) has shown that substitutive reaction chains may be initiated by the additive chlorination of co-present olefins. The inhibitory effect of free oxygen on halogenation reactions, noted by Luther and Goldberg (*8*), was interpreted by Pease and Walz (*9*) to indicate a chain mechanism in the chlorination of methane. The same effect is striking in the chlorination of methane homologs. Presumably the chains are terminated by reaction between the free organic radicals and oxygen.

However the chains are initiated, the reaction occurs homogeneously in vapor phase or in liquid phase. At a given temperature, reaction in liquid phase is much more rapid, as would be expected; even at temperatures as low as 150° C. in the dark, reaction proceeds rapidly to completion.

Chlorination Rule 6

Excessive temperatures and/or reaction times result in appreciable pyrolysis of the chlorides in the order primary < secondary < tertiary.

This has already been commented on in connection with rule 3 in so far as excessive temperatures are concerned, but it may be added that the extent of the pyrolysis is more than would be predicted from data obtained by passing the pure chlorides through a hot reactor (*12*) in the absence of chlorine. The free radical formation already postulated would be expected to lead to this result, since the radicals may decompose as follows:

$$R \rightarrow C_nH_{2n} + H$$

The free hydrogen atoms would continue the chlorination chain as follows:

$$H + Cl_2 \rightarrow HCl + Cl$$

In order to study the effect of abnormally long reaction times, the following experiment was performed:

> A mixture containing approximately 2 moles of pentane to a mole of chlorine was produced by bubbling chlorine slowly through *n*-pentane maintained at 25° C. in a flask in the absence of light. The gaseous mixture was allowed to sweep out the air from a 3-liter flask the neck of which had been drawn to a tip; after the air was considered to have been expelled from the flask, it was sealed. The flask and contents were maintained at 100° C. continuously for 5 days in order to complete the reaction in the absence of light. Analysis of the product by a Weston microcolumn showed a much larger ratio of polychlorides to monochlorides than was obtained in a control experiment where the reaction was allowed to take place rapidly in the presence of light. The *K* of rule 7 was 1.53 for the control test as against 0.3 for the reaction in the dark. This excessive polychloride formation was presumably caused by the following reactions:

$$C_5H_{11}Cl \rightarrow C_5H_{10} + HCl^*$$
$$C_5H_{10} + Cl_2 \rightarrow C_5H_{10}Cl_2, \text{ etc.}$$

It is interesting to note that, contrary to a prediction in the literature (*1*), monochlorides were definitely present even under these extreme conditions.

Chlorination Rule 7

If a molar excess of hydrocarbon is used and the chlorination conditions are maintained constant, the yield of monochlorides *vs.* polychlorides may be obtained from the equation:

$$X = KY$$

where X = weight ratio of monochlorides over polychlorides
Y = ratio of moles of hydrocarbon over moles of chlorine
K = a constant peculiar to the hydrocarbon and the conditions

As evidence, Figure 3 is presented. In applying this graph, conditions are chosen so that the chlorine all reacts.

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* Definite evidence that this reaction proceeds slowly at 100° C. has been obtained during the distillation of the chlorides of *n*-pentane.

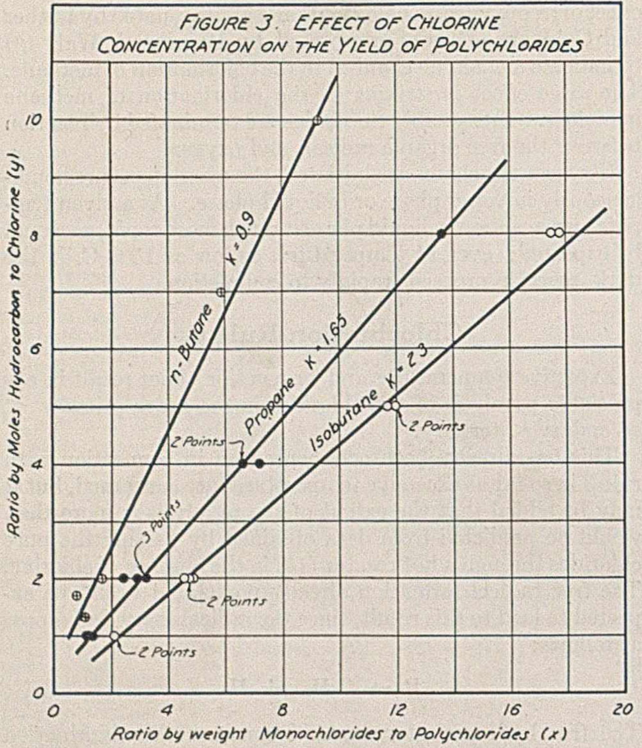


FIGURE 3. EFFECT OF CHLORINE CONCENTRATION ON THE YIELD OF POLYCHLORIDES

The practical import of rule 7 is that the yield of overchlorinated material may be suppressed to any desired degree if only a small percentage of the material to be chlorinated is allowed to react at each pass through the chlorinator. This applies to any stage of chlorination. The idea that there is a strong, inherent tendency toward complete chlorination has not been supported by these experiments on the paraffins of three, four, and five carbon atoms although there is evidence that the statement is true in the case of methane, which, in contrast to its homologs, is less reactive in every way.

An economic balance must be struck between the advantages of the higher yields of monochlorides which are caused by the lower chlorine concentrations in the reacting hydrocarbon, and the increased cost of additional recycling. When chlorination is achieved thermally, recycling involves the expense of heating and cooling large quantities of materials. In the case of the further thermal chlorination of the homologous alkyl chlorides, too many passes through the hot reactor may increase the amount of pyrolysis unduly, so that too much recycling is undesirable from that standpoint also.

One of the advantages of liquid-phase thermal chlorination is that, because of the lower temperatures involved, the pyrolysis is almost completely eliminated and the amount of heat put into the reacting materials and removed from the reaction products is lessened.

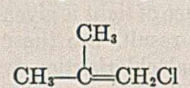
Chlorination Rule 8

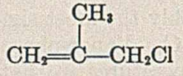
Dichlorination proceeds by two mechanisms: (1) loss of hydrogen chloride followed by addition of chlorine to the resulting olefin and (2) progressive substitution. Slow, thermal chlorination favors mechanism 1, whereas with rapid, liquid-phase or vapor-phase, single-pass thermal reaction, or low-temperature photochemical conditions, mechanism 1 is substantially eliminated.

In view of the large amount of work which has been performed on the addition of chlorine to olefin bonds, it is evident that conditions conducive to the formation of unsaturates must result in at least some union of chlorine with these products, unless the temperature is too high. Thus, as already mentioned, a vapor-phase thermal chlorination of *n*-pentane at 100° C. yields a much higher ratio of polychlorides to monochlorides than if the reaction is carried out rapidly at the same temperature in the presence of light. This is due to the pyrolysis of the secondary chlorides which, though very slow, is appreciable at this temperature, followed by saturation of the double bonds with chlorine.

Under conditions of rapid thermal chlorination some pyrolysis is apt to occur, but the resulting olefins largely escape reaction unless they are recycled. If they are recycled by a process in which the chlorine is mixed with hydrocarbon at relatively low temperature and the mixture is subsequently heated to bring about reaction, there is an appreciable evolution of heat at the point of mixing where the chlorine adds to olefin bonds. The writers have condensed out high-boiling chlorides formed at the place of mixing the recycle gases with chlorine. These were, at least in part, formed by the additive chlorination of olefins and chloroölefins.

Kondakoff (*6*) has shown, however, and his findings have been repeatedly confirmed, that olefins which react readily with mineral acids (usually those capable of thus forming tertiary halides) yield substitution products in addition to, or instead of, undergoing addition. Thus isobutene yields isocrotyl chloride and isobutenyl chloride, with the following structures, respectively:


$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2Cl$


$CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2Cl$

At higher temperatures there is an increasing tendency for chlorine to substitute rather than to add to olefins, so that even normal alkenes may yield largely chloroölefins rather than dichlorides if they are recycled in a process which heats the material to be chlorinated to reaction temperature and then mixes it with chlorine. Under these conditions there is no opportunity for the chlorine to react with the unsaturated compound at low temperature.

With rapid, liquid-phase, thermal chlorination the chlorine disappears with such extreme rapidity, at temperatures (150° to 200° C.) at which pyrolysis is not appreciable within the time interval involved, that no olefins are formed. The crude reaction product is often water-white under these conditions. Obviously, no dichlorination can occur by mechanism 1 of rule 8 when this is true. The same thing may be said of low-temperature photochemical chlorination.

Conclusive evidence that dichlorination occurs by progressive substitution is available in the formation of large quantities of 1,3-disubstitution products which cannot be produced by the addition, under these conditions, of either hydrogen chloride or chlorine to any olefin or chloroölefin. These products are to be discussed further later in the paper.

Chlorination Rule 9

In vapor-phase chlorination the presence of a chlorine atom on a carbon atom tends to hinder further reaction upon that carbon atom during the second substitution.

The data obtained in the dichlorination of propane and isobutane will be presented in a subsequent paper. Only small amounts of dichlorides containing both chlorine atoms on the same carbon atom are found to be present. In the case of propane the boiling points of the dichlorides are as follows: 2,2-dichloride, 69.7° C.; 1,1-dichloride, 86° C.; 1,2-dichloride, 96.8° C.; 1,3-dichloride, 120.4° C. A rectification analysis is therefore conclusive and relatively easy.

Most organic chemists with whom the writers discussed rule 9 expressed surprise. Chlorine is usually regarded as a highly "negative" substituent, and the presence of such a linkage usually activates the other atoms or groups attached to the same carbon atom. Other negative groups, such as phenyl or carboxyl, activate hydrogen atoms for substitution. Thus, ethylbenzene shows a strong tendency to chlorinate in the alpha position, only about 10 per cent substituting in the beta position at room temperature and about 45 per cent at 500° C., whereas a nonselective chlorination requires a yield of β-phenylethyl chloride amounting to 60 per cent of the monochlorides substituted on the side chain.

Perhaps the situation here is complicated by intramolecular rearrangement subsequent to dichlorination or possibly the chlorine does not behave as a negative group in this case.

Chlorination Rule 10

Herzfelder's rule (1893), "when into a monohalogen compound a second halogen is introduced, it always attaches itself to that carbon atom which is situated next to the carbon atom already united with halogen," does not apply to chlorinations and must be replaced in this field by rules 1 and 9.

This is obvious from rule 9. With isobutane the yield of 1,3-dichloride is so great that this compound ordinarily composes more than half of the dichloride fraction. Not even half of the material reacts according to Herzfelder's rule in spite of the fact that both monochlorides of isobutane can be chlorinated to the 1,2-derivative and the tertiary chloride can yield only the 1,2-dichloride on further substitution.

So far, no method has been devised for calculating yields of dichlorides from the monochlorides. The presence of chlorine seems to exert a disturbing influence on the relative reaction rates of the hydrogen atoms in the molecule. Further work may lead to an elucidation of these relationships.

Acknowledgment

This work has been made possible by funds provided by J. K. Lilly, The Cleaner Corporation of America, and the Mallinckrodt Chemical Works, Purdue Research Foundation Fellowships 1, 15, 16, and 35. The writers wish to thank Lee Clark and John Olin of the Sharples Solvents Corporation for certain samples and for duplicate analyses.

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Received September 2, 1935. This paper contains material extracted from the Ph.D. theses of Paul Weber and E. T. McBee.

Phosgene

● In the Analytical Edition [8, 20 (1936)] those interested in the question of whether or not phosgene may be present in gases from fires extinguished with carbon tetrachloride will find an interesting contribution to the subject. It has to do with phosgene in gases from experimental fires extinguished with carbon tetrachloride fire-extinguisher liquid and presents the results of coöperative work by W. P. Yant, J. C. Olsen, H. H. Storch, J. R. Littlefield, and Leopold Scheflan.

Nitration of Gaseous Paraffins[1]

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The nitration of saturated hydrocarbons has been recently reviewed (3). So far as the writers are aware, no industrial application has been made of this reaction. There is no record in the literature, prior to the present work, of the nitration of any saturated hydrocarbon of less than five carbon atoms, and nitration reactions had been effected practically exclusively in the liquid phase.

The saturated hydrocarbons of less than five carbon atoms have critical temperatures lower than the temperature of reasonably rapid nitration, and all organic solvents, otherwise suitable as media for the reaction, are attacked under these conditions. It is therefore desirable to operate in vapor phase.

The results obtained in this laboratory during several years of study of the vapor-phase nitration of paraffins are reviewed. Nitromethane, nitroethane, both nitropropanes, and all four nitrobutanes are readily obtainable. Ratios of isomers in the reaction products are controllable to a considerable extent. These compounds are colorless, relatively nontoxic, stable solvents boiling from 101° to 151° C. Their physical and chemical properties, possible uses, and the economics of their production are reviewed.

NITROPARAFFINS were first produced in 1872 by Meyer (*11*) who prepared them by the reaction which bears his name—i. e., metathesis of an alkyl halide with silver nitrite. Although Beilstein and Kurbatow (*1*) obtained mononitrocyclohexane in 1880 by the nitration of a petroleum fraction, the nitration of paraffin hydrocarbons was first studied in the years between 1892 and 1907. Except for a patent issued to Hopkins (*8*) in 1926, there is little evidence in the literature that the industrial application of this reaction has been attempted. Gruse (*7*) stated in 1928: "The nitration of petroleum fractions has been studied to some extent but no results of either scientific or technical importance have been obtained because of the mixed nature of the fractions and the complexity of the reactions."

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[1] This paper is the fourth in a series on the subject of syntheses from natural gas hydrocarbons.

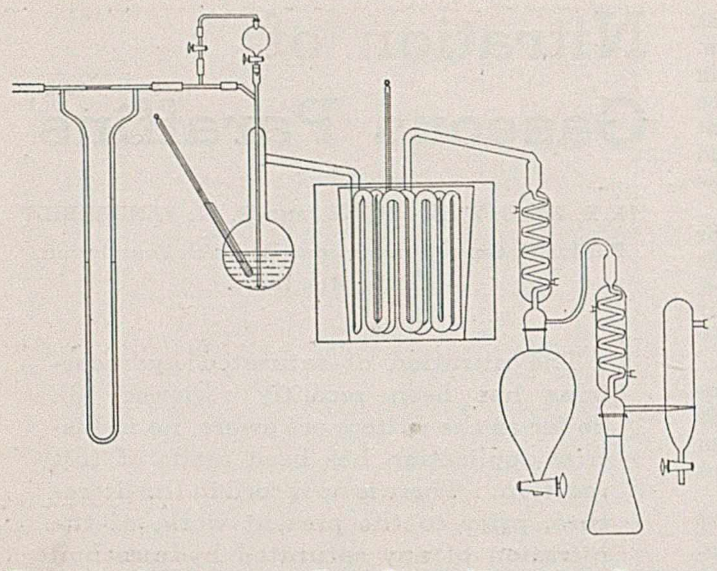


FIGURE 1. APPARATUS FOR VAPOR-PHASE ATMOSPHERIC PRESSURE NITRATION OF PARAFFIN HYDROCARBONS

In spite of this discouraging situation the study of the nitration of the gaseous paraffins was begun in this laboratory in 1930 because of the following considerations: (1) the abundance and low cost of the simpler paraffin hydrocarbons which are available in a condition of high purity, (2) the paucity of the modes of chemical attack to which these hydrocarbons are susceptible, (3) the absence from the literature of any recorded nitration of saturated hydrocarbons of less than five carbons atoms, (4) the fact that nitric acid can be produced by the oxidation of synthetic ammonia at a cost of approximately 1.75 cents per pound (anhydrous basis), and (5) indications in the literature that these compounds would be of value if they could be produced at a low cost.

Technic of Nitration of Gaseous Hydrocarbons

The hydrocarbons of less than five carbon atoms have not been nitrated by previous workers. The reason for this is, presumably, that nitration is thought of as a liquid-phase reaction, and these hydrocarbons have critical temperatures lower than the temperature of reasonably rapid reaction. Acetic acid has been recommended as a mutual solvent in the nitration of paraffins, but it has also been observed that the lower members of the methane series are more resistant to all forms of chemical attack than are their higher homologs. It was found that, as a result of this tendency, conditions suitable for the nitration of even the butanes caused serious oxidation of the acetic acid by nitric acid. Other organic compounds which might serve as mutual solvents for the hydrocarbon and nitric acid are even more readily oxidized under these conditions than is acetic acid.

It is evident then, that reaction must be effected, if at all, in the vapor phase. According to the literature, nitric acid vapor is completely decomposed at 250° C. or higher into nitric oxide, nitrogen dioxide, water, and oxygen. The only prospect of successful nitration seemed to exist in the possibility that at these elevated temperatures the nitration reaction would be so much accelerated that it would take place before the decomposition of the nitric acid had proceeded too far. This proved to be the case.

Liquid-phase nitration of saturated hydrocarbons has always been difficult (even when pure starting materials were available) because nitric acid and the hydrocarbons are mutually insoluble, while the nitrated product is considerably more soluble in the nitric acid layer than is the hydrocarbon, and is there subjected to further nitration and oxidation. By operating in vapor phase, the reagents may be immediately mixed in any desired proportion; reaction is extremely rapid (nearly complete in less than one second), and substantially no polynitro derivatives are formed.

The nitration apparatus used in this laboratory for the routine production of nitroparaffins is illustrated in Figure 1:

Hydrocarbon vapor passes at the rate of 150 liters per hour through the flowmeter and through hot, concentrated nitric acid contained in the flask. The mixture of hydrocarbon and nitric acid vapors then passes through the reactor, which is made of 10-mm. glass tubing and consists of a series of U-bends. Its capacity is 280 ml. This reaction tube is heated by immersion in a eutectic mixture of sodium nitrite and potassium nitrate. Most of the product condenses in the first condenser and collects in the dropping funnel, while part of it collects in the Erlenmeyer flask. Both the flask and dropping funnel are cooled by immersion in ice water. A fog trap, modeled after that of Blackie (*2*), serves to remove a small additional amount of nitroparaffin. Ground-glass connections are used wherever nitric acid is present.

The operation is as follows:

The nitrate-nitrite bath is brought to a temperature of 420° C. Temperature is observed by means of a nitrogen-filled thermometer. The hydrocarbon vapor is started through the nitric acid, and the latter is heated to 108° C. This temperature insures a molar ratio of hydrocarbon to nitric acid of about 2 to 1. It is important that no large amount of nitrogen dioxide should be present in the nitric acid at any time, since this volatile compound may be rapidly removed from the nitric acid by the sweeping-out action of the hydrocarbon vapor and thus form an explosive mixture with it. An explosion was thus produced in one of the early experiments when fuming nitric acid was used and at another time when the nitric acid had been heated to 106° C. without any gas being bubbled through it. Otherwise no explosions have occurred at any time during this work, and it is not believed that these nitrations present any serious hazards if the directions are observed. During the run the hydrocarbon keeps the nitrogen dioxide effectively swept out of the nitric acid.

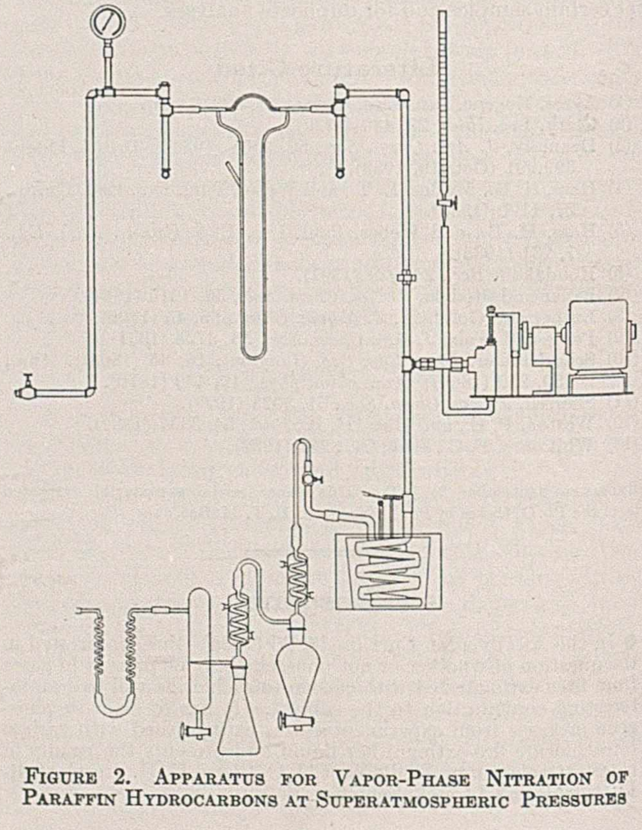


FIGURE 2. APPARATUS FOR VAPOR-PHASE NITRATION OF PARAFFIN HYDROCARBONS AT SUPERATMOSPHERIC PRESSURES

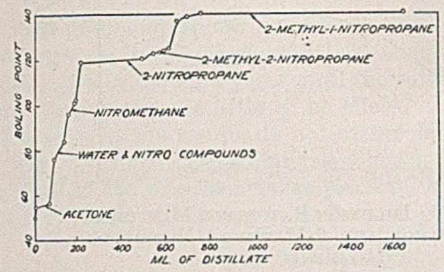


FIGURE 3. RECTIFICATION CURVE OF PRODUCT MADE BY NITRATING ISOBUTANE AT 420° C.

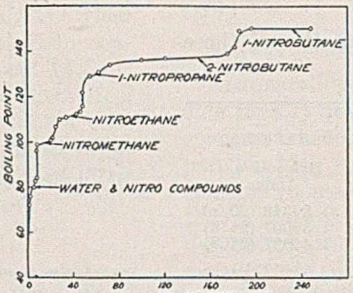


FIGURE 4. RECTIFICATION CURVE OF PRODUCT MADE BY NITRATING BUTANE AT 420° C.

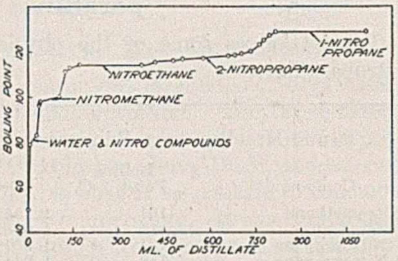


FIGURE 5. RECTIFICATION CURVE OF PRODUCT MADE BY NITRATING PROPANE AT 420° C.

The height of the nitric acid in the flask is maintained fairly constant by additions from the dropping funnel; the latter is refilled as desired. At the end of a run the hydrocarbon vapor is washed out of the apparatus by means of nitrogen.

The product separates into two layers; the lower one consists essentially of very dilute nitric acid, and the nitroparaffins are present in the upper layer.

It is evident that the unreacted hydrocarbon and other gases which are present carry out with them an appreciable amount of nitroparaffin vapors. When the object of the experiment is simply to produce nitroparaffins for further study, this loss is unimportant, but in certain experiments where the effect was studied of a large excess of hydrocarbon upon the course of the reaction it was necessary to avoid this loss, which naturally increases with a greater excess of hydrocarbon.

For this purpose a smaller scale apparatus was employed:

The flask containing the nitric acid was heated in a stirred oil bath, the temperature of which was controlled by means of a thermoregulator. The temperature of the salt bath was also controlled by means of a thermoregulator. After traversing the condensers, the gases from the reaction were led through a U-tube surrounded by an ice-salt mixture, and then to an insulated 500-ml. flask which was at the bottom of a scrubbing column. A hydrocarbon reflux was maintained in the scrubbing column by means of dry-ice cooling. After each run the hydrocarbon in the 500-ml. flask was distilled off slowly through the column while a good reflux was maintained, and in this way the nitroparaffins were completely recovered.

After each run the nitric acid flask was cooled to room temperature and the level of the contents brought to the original height by adding acid from a buret. This enabled the operator to determine the nitric acid used. Unreacted nitric acid was determined by titration of the aqueous product layer.

The apparatus for studying the reaction under superatmospheric pressure (Figure 2) was similar to that shown in Figure 1 except that the hydrocarbon entered the reactor under a fraction of its own vapor pressure, the nitric acid was forced into the reactor by a Hills-McCanna stainless-steel pump (No. S M4 × 10, piston diameter $^5/_{16}$ inch or 0.8 cm.) and the reactor consisted of a stainless-steel coil equipped with fittings of the same alloy.

Composition of Nonaqueous Layers

When isobutane was nitrated at 150° C. in sealed tubes, the product (obtained in 22 per cent yield) was tertiary nitrobutane (2-methyl-2-nitropropane) of 99 per cent purity. This unique compound has a change of freezing point of 27° C. per mole of solute per kg. of solvent (as compared to 1.86° C. for water) so that the purity could be estimated easily from the freezing point of the crude sample. When nitration occurs under atmospheric pressure and at a temperature of 420° C., the products are somewhat more complex. The rectification curves (Figures 3 to 5) were obtained by distilling the mixture (after repeated washing with water and drying) under atmospheric pressure until nitromethane began to come over, after which the distillation was continued at diminished pressure. All boiling points were corrected to 760 mm. for purposes of ready interpretation. The rectifying column was 150 cm. high and 2.8 cm. in diameter, and was packed with glass spirals described by Wilson, Parker, and Laughlin (*13*). It was efficiently insulated, and of the total-condensing variable take-off type. Table I summarizes the results of these analyses.

The figures in the last column to the right are based upon the nitric acid consumed in the reaction. They do not represent the maximum yields obtainable, since they are based upon experiments in which there was only a 2 : 1 molar excess of hydrocarbon over nitric acid, and there was some loss of nitroparaffins in the gases escaping from the reaction. They are believed to indicate pretty closely the relative yields obtainable with these several hydrocarbons.

The striking fact that derivatives of lower homologs are obtained from a given hydrocarbon might be taken to mean that the starting materials were impure. This is not the correct explanation, however, since Podbielniak column analyses always showed a very high purity in the case of propane, butane, and isobutane, which were the Phillips Petroleum Company's C. P. grade. The methane and ethane were obtained from another source and were not nearly so pure, but it is evident from the negative results obtained with methane that any of this compound present in the ethane could not have been a source of serious error. Nitroethane boils so close to 2-nitropropane that the analysis of the product from propane may be considerably in error.

A considerable amount of oxidation accompanies the nitration reaction, and the writers believe that this phenomenon results in the conversion of paraffins to fatty acids which are nitrated in the alpha position and subsequently lose carbon dioxide to yield a lower nitroparaffin. The same net result may be obtained in a number of other ways—for instance, by the combination of a free alkyl radical with a molecule of nitrogen dioxide.

TABLE I. RESULTS OF ANALYSES

Hydrocarbon	Acetone	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	1-Nitroisobutane	2-Nitroisobutane	Yield per Pass
	Per cent									
Methane	.	...	...	..	..	..	..	..	.	0
Ethane	.	10–20	80–90	..	..	..	..	..	.	9
Propane	.	9	(26?)	32	33	..	..	..	.	21
Butane	.	6	12	5	..	27	50	..	.	28
Isobutane	5	3	...	..	20	..	..	65	7	25

Physical Properties of the Eight Simplest Nitroparaffins

Table II gives some of the physical properties of these nitroparaffins.

TABLE II. PHYSICAL PROPERTIES OF NITROPARAFFINS

Compound	Boiling Point, ° C.	Density	Refractive Index
Nitromethane	101	1.1382 (20/20)	1.39348 (20/D)
Nitroethane	115	1.0461 (25/25)	1.39007 (24.3)
1-Nitropropane	131	1.0023 (25)	1.40027 (24.3)
2-Nitropropane	118	1.024 (0)	.....
1-Nitrobutane	151	.....	.....
2-Nitrobutane	139	0.9877	.....
2-Methyl-1-nitropropane	140.5	0.9625 (25/25)	1.4050 (25)
2-Methyl-2-nitropropane	126.4 (m. p., 25.6)	0.9501 (28/4)	.....

Identification of Products

Acetone was identified by its boiling point, 56.5° C., and by conversion to dibenzylidene acetone (melting point 110.5° to 111.5° C.), and a mixed melting point with an authentic sample.

Nitromethane was identified by its boiling point, 101° C., and the formation of the potassium salt of methazonic acid on treatment with concentrated potassium hydroxide.

2-Nitropropane was identified by its physical constants, by conversion to the pseudonitrole, and by a Dumas nitrogen determination: Nitrogen found, 16.0 per cent; nitrogen calculated, 15.7.

2-Methyl-1-nitropropane was identified by its boiling point and by the fact that a red color developed when sulfuric acid was added to a solution of the compound in aqueous potassium hydroxide to which sodium nitrite had previously been added (nitrolic acid formation). A Dumas nitrogen determination showed: Nitrogen found, 13.9 per cent; nitrogen calculated 13.6.

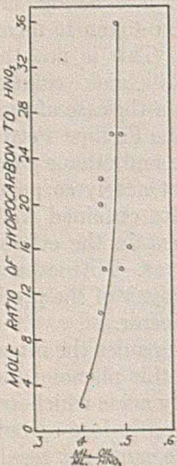


FIGURE 6. EFFECT OF EXCESS HYDROCARBON ON YIELD OF NITROPARAFFIN

2-Methyl-2-nitropropane was obtained in 99 per cent purity by the nitration of isobutane at 150° C. Its unique physical constants were considered to provide conclusive identification in view of its insolubility in concentrated potassium hydroxide solution (absence of primary and secondary nitroparaffins), and the starting materials.

Nitroethane, 1-nitropropane, 1-nitrobutane, and 2-nitrobutane were identified by their physical constants and starting materials.

Reduction Products of Nitric Acid

It is evident that a considerable proportion of the nitric acid is reduced under the conditions of these nitrations. Ordinarily the gaseous products are colorless, indicating the absence of nitrogen dioxide. It was of considerable importance to learn whether the nitrogen was reduced to the elemental form or merely to nitric oxide; in the latter case it could be readily reoxidized to nitric acid, while in the former it would be wasted. As a result of the formulation of complete nitrogen balances it is concluded that, if any free nitrogen is formed in these reactions, it is of the order of 5 per cent or less of the nitrogen entering the reactor as nitric acid vapor. The remainder is present as unreacted nitric acid, nitroparaffins, and nitric oxide.

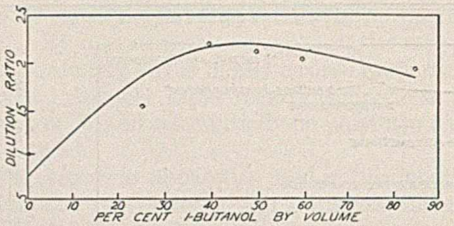


FIGURE 7. DILUTION RATIOS FOR MIXTURES OF 1-BUTANOL AND 2-METHYL-1-NITROPROPANE

Effect of Temperature

Total yields of nitroparaffins are surprisingly constant from 150° to 420° C. when the optimum rate for each temperature is employed. This rate can be determined readily by observing the color of the outlet gases. When the rate is too rapid, some nitrogen dioxide is present. When the brown color of nitrogen dioxide has just disappeared, optimum results are secured. Too long exposure in the reactor may result in a lowered yield because of decomposition of the nitroparaffins. When this happens, a brown deposit is formed in the reactor, although normally the tube is kept perfectly clean by the oxidizing action of the nitric acid.

The ratios of isomeric nitroparaffins vary considerably with changes in temperature. As has been noted in the chlorinations, an increase of temperature results in an increased yield of primary isomers and a decreased yield of the secondary and tertiary derivatives. Thus at 150° C. the nitration of isobutane yields 2-methyl-2-nitropropane as the sole nitrated product; at 420° C. this isomer comprises only about 7 per cent of the nitroparaffins. This difference is probably caused by two factors: (1) the less selective nature of the reaction at high temperatures and (2) the greater stability of the primary isomers under the high temperature conditions. The production of nitro derivatives having a number of carbon atoms fewer than that of the starting hydrocarbon has been observed only at the higher temperatures.

Effect of Free Oxygen

When air or free oxygen is added to the nitration mixture the oxidation reaction is favored with no increase in the nitration. This is probably because the equilibrium

$$4HNO_3 \rightleftharpoons 4NO_2 + 2H_2O + O_2$$

is displaced almost completely to the right at these temperatures and the only reason that nitric acid is present is that it has not had time to decompose. Under these circumstances, no additional formation of nitric acid would be expected when free oxygen is added. On the other hand, it has been shown that oxides of nitrogen are excellent oxygen carriers under these conditions.

Effect of Superatmospheric Pressure

The results of a series of runs with isobutane are as follows:

Temp. of Salt Bath	Length of Run	HNO_3 Used	Rate of Flow of Hydrocarbon	Upper Layer	HNO_3 Recovered	Ratio, Upper Layer: HNO_3 Used	Abs. Pressure
° C.	*Min.*	*Ml.*	*Liters/hr.*	*Ml.*	*%*	*Ml.*	*Lb./sq. in.*
340	30	22.4	55	7.4	8	0.33	14.5
304	40	11.3	34	4.0	..	0.35	14.5
290	30	28.5	64	14.5	7	0.51	41
290	30	33.6	64	16.4	14	0.49	41

In addition to increasing the yield somewhat, the use of superatmospheric pressure results, as would be expected, in a large increase in reaction rate. The nitration is presumably a second-order reaction.

Effect of Excess Hydrocarbon

The results are shown graphically in Figure 6. The yield of nitroparaffin increases with increasing hydrocarbon concentration in the inlet gases until the ratio is about 14 to 1, after which there is little or no effect. It is of theoretical interest that the results do not extrapolate to 100 per cent yield of nitroparaffins at infinite dilution. This means that not all of the oxidation takes place by the action of nitric acid or oxides of nitrogen upon the nitroparaffin.

Effect of Catalysts

No catalyst has been found which increases the yield of nitroparaffin. Aluminum nitrate seems to have no effect. This is also true of glass and stainless steel. Silica gel and platinum promote oxidation rather than nitration. With the former, considerable amounts of acetic acid are formed. This is a normal component of the aqueous product layer and was identified by conversion to aceto-*p*-toluidide.

Material Cost of Production of Nitroparaffins

Yields of 40 per cent per pass have been obtained in the nitration of the butanes. Since not more than 5 per cent of the nitric acid is reduced to free nitrogen, this means a net, over-all yield of $(40 \times 100)/(40 + 5)$ or 89 per cent, based upon nitric acid, assuming that the nitric oxide can all be reconverted to nitric acid. The hydrocarbon which is not nitrated is converted to carbon monoxide, carbon dioxide, and water. This reaction requires something like seven moles of nitric acid for each mole of butane. Since about 60 per cent of the nitric acid is used as oxidizing agent, about one-seventh of 60 per cent or 0.08 mole of hydrocarbon is oxidized by the nitric acid for each mole of nitric acid reacting. The percentage of hydrocarbon nitrated is therefore approximately $(0.40 \times 100)/(0.40 + 0.08)$ or 83 per cent.

Nitric acid can be produced by the oxidation of ammonia at a cost of approximately 1.75 cents per pound on an anhydrous basis. Butane is available at about 0.6 cent per pound. The raw material cost of a pound of crude, nitrated butane, using the above figures, is approximately 1.8 cents per pound.

It is too early to estimate the other costs of the process, but it seems a safe conclusion that nitroparaffins can be produced cheaply if a large-scale use should develop. A review of the possible uses of these compounds is therefore in order.

Toxicity of Nitroparaffins

The prefix "nitro" suggests high toxicity to a chemist. It was shown, however, as long ago as 1891 (*6*) that nitromethane, when injected into a dog, exhibited less toxicity than 1-butanol. Preliminary tests by Henry F. Smyth, Jr., of the Laboratory of Hygiene, Philadelphia, made upon white rats and guinea pigs, with a sample of nitrated propane furnished by this laboratory led to the conclusion that "the vapors are considerably less toxic than any of the materials listed above (benzene, aniline, carbon disulfide, carbon tetrachloride, and nitrobenzene), and ... we believe that this nitromixture is safe to use in reasonable proportions in lacquers."

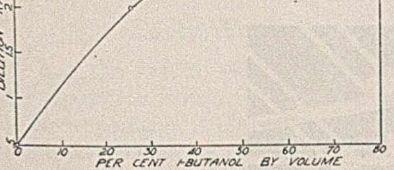


FIGURE 8. DILUTION RATIOS FOR MIXTURES OF 1-BUTANOL AND 2-METHYL-2-NITROPROPANE

Odor, Color, Stability, and Corrosiveness

Nitroparaffins have a characteristic, mild, not unpleasant odor usually described as chloroform-like. They are entirely colorless when pure. A sample of tertiary nitrobutane prepared in May, 1931, is still colorless (June, 1935), and has not changed in melting point, so that it seems safe to conclude that it is stable at ordinary temperature. It has been found desirable, however, to use diminished pressure when the nitroparaffins are subjected to prolonged rectification.

In the A. S. T. M. corrosion test, the polished copper strip lost practically none of its polish, but a very slight white "bloom" was visible if it was viewed from the proper angle. A strip from a tin can immersed for 7 months in a 50–50 mixture of 1-butanol and 2-methyl-1-nitropropane has shown no signs of corrosion.

Data Concerning Suitability as Ingredients of Pyroxylin Lacquers

As long ago as 1907 Fischer (*4*) patented the use of nitromethane as a solvent for cellulose nitrate and cellulose acetate. Hopkins and Buc (*9*) pointed out in 1928 the possibility of using as nitrocellulose solvents mixtures of alcohols and nitrated derivatives of petroleum hydrocarbons of from six to twelve carbon atoms. So far as known, however, these compounds have not been applied for this purpose, probably because nitromethane has been too expensive, and the nitroparaffins of from six to twelve carbon atoms are less volatile than the common lacquer solvents; for instance, 1-nitrohexane boils at 193° to 194° C.

It is evident from Table II that solvents which boil from 101° to 151° C. can be obtained by the nitration of propane and the butanes. This range includes many of the medium-boiling and high-boiling lacquer solvents. Tests were therefore made to determine the suitability of these nitroparaffins for this purpose.

The dilution ratios were run according to the directions of Gardner (*5*). The results are given for a 10 per cent final concentration of nitrocellulose. It is evident from Figures 7 and 8 and the following table that, while pure 2-methyl-1-nitropropane and 2-methyl-2-nitropropane are not very powerful pyroxylin solvents, the addition of an alcohol—for example, 1-butanol—produces mixtures which have dilution ratios equal or superior to those of the ester solvents (butyl acetate and amyl acetate) of about the same boiling point:

Solvent	Nonsolvent	Dilution Ratio
Butyl acetate	Toluene	2.7
25% 2-methyl-2-nitropropane 75% 1-butanol	Toluene	2.9
Amyl acetate	Toluene	2.2
60% 2-methyl-1-nitropropane 40% 1-butanol	Toluene	2.2

Dilution ratios with petroleum distillates as the nonsolvent are less favorable to the nitroparaffins than when toluene is used.

The solubility behavior of some resins in 2-methyl-1-nitropropane and in a 50–50 mixture of 2-methyl-1-nitropropane with 1-butanol is shown in the following table; all of these resins except shellac were completely soluble in the mixture:

Resin	Behavior in Nitroparaffin	Behavior in Mixture
Rosin	Dissolved slowly	Dissolved rapidly
Ester gum	Dissolved rapidly	Dissolved rapidly
Elemi	Insoluble	Dissolved rapidly
Resinel-2	Insoluble	Dissolved slowly
Shellac	Insoluble	Slightly soluble
Mastic	Slightly soluble	Dissolved slowly
Manila	Slightly soluble	Dissolved slowly
Kauri	Slightly soluble	Dissolved slowly
Dammar	Slightly soluble	Slightly soluble
Copal	Slightly soluble	Dissolved slowly

The evaporation rates of nitroparaffins were found to be almost identical with those of the ester solvents of the same boiling point. The solubility of water in nitroparaffins is low. For instance, water is soluble in 2-methyl-2-nitropropane to the extent of about four parts per thousand. We might therefore expect satisfactory blush resistance. To test this, two lacquers were made up which had identical compositions except that butyl acetate was used in one, and the other contained, in place of the butyl acetate, a mixture of 2-methyl-1-nitropropane and 1-butanol. No difference could be observed in the blushing tendencies of the two lacquers; whenever one of them blushed, the other also blushed.

Flash Point and Explosibility

1-Methyl-2-nitropropane has a flash point (determined by the Penske-Martin closed-cup apparatus) of 13° C. Nitroparaffins are said to be explosible, although with difficulty. This is doubtless true of nitromethane and of certain of the polynitro derivatives of methane homologs, but attempts to explode nitroethane and its higher homologs have been uniformly unsuccessful. Tests upon nitroethane and nitropropane were kindly carried out by W. E. Lawson, of the Eastern Laboratory of E. I. du Pont de Nemours & Company. The tests were made on lead blocks in the usual manner. The height of the liquid was 2 inches (5.08 cm.) and the diameter was the same. No. 8 electric blasting caps were used and, when negative results were obtained, the nitroethane was once more tested at 96° C., again with negative results. Burning and dropping upon red hot wire coils also failed to produce an explosion.

It seems highly probable that nitroparaffins will find a place in the pyroxylin industry if the process cost in their manufacture is not excessive.

Use in Diesel Fuels

One of the points about Diesel fuel which is alleged to be troublesome is the inability to obtain a sufficiently low temperature of ignition. Various patents have been taken out in this country and abroad on the addition of priming compounds to these fuels. Loomis (*10*) has patented the use of nitroparaffins for this purpose, added in a proportion of less than 5 per cent. This represents a possible application of these compounds.

Solvent Refining of Lubricating Oils

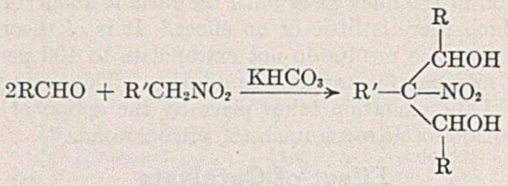
The use of nitrobenzene for this purpose suggested the possibility of utilizing nitroparaffins. Preliminary tests by the Phillips Petroleum Company indicate that these solvents are of value in this field.

Raw Materials for Organic Syntheses

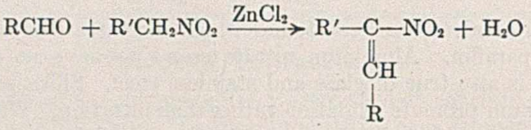
The nitroparaffins are surprisingly reactive compounds. The primary isomers can be hydrolyzed with concentrated hydrochloric acid to form fatty acids and hydroxylamine hydrochloride:

$$\mathrm{RCH_2NO_2 + HCl + H_2O \longrightarrow RCOOH + NH_2OH{\cdot}HCl}$$

Alkaline reduction yields aldehydes from the primary isomers and ketones from the secondary nitroparaffins. Acid reduction yields amines. Condensation of aldehydes with primary and secondary nitroparaffins yields either nitroalcohols or nitroölefins, depending upon conditions:



$$\mathrm{2RCHO + R'CH_2NO_2 \xrightarrow{KHCO_3} R'{-}\underset{\underset{\underset{R}{|}}{CHOH}}{\overset{\overset{\overset{R}{|}}{CHOH}}{C}}{-}NO_2}$$



$$\mathrm{RCHO + R'CH_2NO_2 \xrightarrow{ZnCl_2} R'{-}\underset{\underset{\underset{R}{|}}{CH}}{\overset{}{\underset{\|}{C}}}{-}NO_2 + H_2O}$$

Acid reduction of the nitro alcohols yields amino alcohols.

Conclusion

The chemical utilization of the gaseous paraffins which, at present, are being wasted in enormous quantities, has been hindered because of the paucity of the modes of chemical attack to which they are known to be susceptible. Vapor-phase nitration constitutes a novel approach to this problem and renders more readily available thousands of old and new compounds of the most varied properties. The commercialization of these processes is being energetically developed.

Acknowledgment

The authors wish to express thanks to the Phillips Petroleum Company and to the Purdue Research Foundation for financing a large part of this research as Fellowship No. 24. A patent which covers broadly the vapor-phase process of nitrating saturated hydrocarbons, and other patents pending and to be applied for, are assigned to the Purdue Research Foundation.

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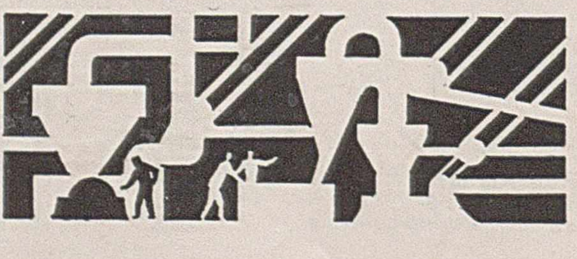

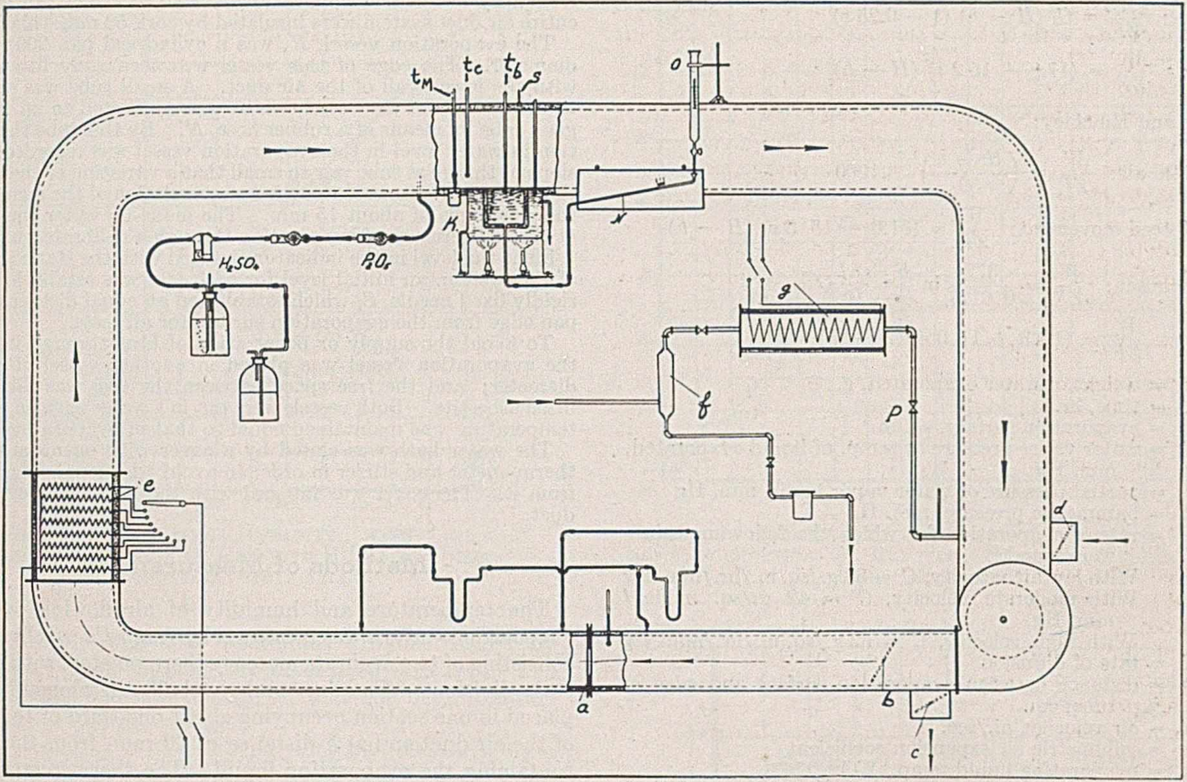

FIGURE 1. DIAGRAM OF VENTILATION SYSTEM

EVAPORATION FROM FREE WATER SURFACE

THE process of evaporation from a free water surface has attracted the attention of scientists for a long time. The different factors affecting this process can be analyzed only through experimental work. Not only the process of cooling air by water and cooling water by air, but the whole design of air-conditioning apparatus, scrubbers, and cooling towers, especially drying apparatus, etc., is dependent on the knowledge of the laws of evaporation from a free water surface.

The subject has been studied by many investigators, many of whom used primitive apparatus or low air temperatures and unreliable methods of measurement. This laboratory started a series of experiments on the subject in 1925 which, after the equipment was redesigned, was completed in 1929 and further extended in 1934.

Early Work

Dalton (*4*) was the first to establish experimentally the basic law of evaporation from free water surfaces—namely, that the rate of evaporation is proportional to the difference between the pressure of the water vapor at the temperature at which it evaporates and the partial pressure of water vapor in the air. Dalton's formula does not include any factor involving rate or direction of air flow.

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Stefan (*11*), Schirbeck (*9*), Trabert (*13*), Carrier (*1*, *2*), Coffey and Horn (*3*), Himus and Hinchley (*5*), Thiesenhusen (*12*), and Rohwer (*8*) have given some empirical equations expressing their experimental results. The tabulation of their formulas is as follows:

Dalton: $$\frac{W}{ZF} = C\,\frac{H-h}{b}\,760$$

Stefan: $$\frac{W}{ZF} = \frac{K}{l}\ln\frac{b-h}{b-H}$$

Schirbeck: $$\frac{W}{ZF} = \frac{K'}{l}\,(l+\alpha t'_m)\,\sqrt{v}\,\ln\frac{b-h}{b-H}$$

Trabert: $$\frac{W}{ZF} = K''\,(l+\alpha t'_m)\,\sqrt{v}\,(H-h)$$

Bigelow: $\frac{W}{ZF} = C_1 (H - h) (1 - 0.25\, v)$

Carrier: $\frac{W}{ZF} = (17.8 + 15.2\, v) (H - h)$

Himus and Hinchley:

for still air: $\frac{W}{ZF} = \left(\frac{H - h}{50}\right)^{1.2} .1000$

for forced movement: $\frac{W}{ZF} = (31.0 + 13.\ 5\, v) (H - h)$

Thiesenhusen: $\frac{W}{ZF} = \frac{372}{0.0127} \ln \frac{b - h}{b - H} \sqrt{v}$

Rohwer: $\frac{W}{ZF} = (18.3 + 11.0\, v) (H - h)$

where W = weight of water evaporated, g.
Z = time, hr.
F = evaporation surface, sq. m.
H = water vapor pressure at temp. of liquid evaporated, mm. Hg
h = partial pressure of water vapor in air, mm. Hg
b = barometric pressure, mm. Hg
C = rate of evaporation for which the following values were found:
With low air velocity, C = 33 g./sq. m./hr./mm. Hg
With moderate velocity, C = 42 g./sq. m./hr./mm. Hg.
With high velocity, C = 52 g./sq. m./hr./mm. Hg
K = rate of diffusion
l = distance between evaporation surface and edge of tube, cm.
v = air velocity, m./sec.
α = volumetric air expansion coefficient
t'_m = evaporating liquid temp., ° C.
C_1 = rate of evaporation depending on air humidity and evaporation surface

Lewis (*6*) showed that for the adiabatic interaction of air and water vapor the ratio of the heat transfer coefficient to the diffusion coefficient is constant and equal to the specific heat of the air. Consequently, if the heat transfer coefficient can be evaluated, the other terms in most of the heat balance or material balance equations that might be written may be evaluated.

Experimental Procedure

The experiments carried out by this laboratory were performed at 40° to 225° C. with a variation in moisture content of dry air from 10 to 250 grams per kg. dry air and of air velocity from 1.0 to 7.5 meters per second.

Further, an essential feature of this work was that heat was supplied only through the evaporation surface or under adiabatic conditions; that is, the interaction of air and free water surface was studied without any complicating factors.

For the experiments on evaporation from free water surfaces, a special ventilation system was designed which consisted of a closed ventilation system with a partial air exchange:

A fan and a ring-shaped air duct (Figure 1) had a circular section for a distance of about 5 meters and a square section of 300 × 300 mm. for about the same length. The air velocity was measured by a sharp-edged orifice *a*, inserted in the middle part of the circular section of the air duct, and it was controlled by means of a butterfly valve, *b*. The rate of circulating air exchange was controlled by means of baffles *c* and *d*.

The air was heated to a given temperature by means of an electric heater, *e*. Temperature control was carried out by switching on the necessary number of sections; one of these had an additional resistance which permitted it to maintain the given temperature fairly closely. Saturation of the circulating air was accomplished by letting in a corresponding amount of superheated steam.

To have a uniform air saturation, the steam was admitted before the fan and passed first through a water separator, *f*, and an electric superheater, *g*. The amount of steam supply was controlled by means of a conventional valve, *P*. The fan and the entire air duct system were insulated by cork 50 mm. thick.

The evaporation vessel, *K*, was a cylindrical pan 200 mm. in diameter. The edge of this vessel was accurately fitted, even with the lower wall of the air duct. A small tube was soldered to the bottom of the vessel, which was connected to an inclined glass tube by means of a rubber hose, *N*. By this tube the variation in water level in the evaporation vessel was recorded. The slope of this glass tube was so small that a variation of the level in the vessel of 1 mm. corresponded to a variation of the meniscus in the glass tube of about 15 mm. The make-up water was added at the temperature of evaporation through a calibrated buret.

Since the level in the indicator changed with the static pressure of the system, an initial level for each test was established by a rigidly fixed needle, *S*, which established an equal distance of the pan edge from the evaporation surface for all tests.

To avoid the supply or penetration of heat through its walls, the evaporation vessel was placed in another vessel of a large diameter; and the free space between the two was filled with dried asbestite. Both vessels were put in a water bath, in which a temperature was maintained equal to that of evaporating water. The water bath was closed by a cover with openings for the thermometer and stirrer in order to avoid additional evaporation from it. The cover was integral with the lower wall of the air duct.

Methods of Measurement

The temperature and humidity of air flowing over the evaporation surface was measured by August's psychrometer, consisting of two accurate mercury thermometers with 0.1° C. scale divisions. The dry- and wet-bulb thermometers were placed in one section occupying about one-third of the width of the air duct and at a distance of 50 mm. from the vessel containing the evaporating liquid. The thermometers used had P. T. R. certificates. The muslin of the psychrometer wet bulb was immersed in a small reservoir inserted in the lower wall of the air duct. The temperatures read were corrected for the emergent stem. This correction for the wet-bulb thermometer was made twice, since its mercury column was partly in contact with the air in the system and partly with that of the room.

The humidity of the air flowing over the evaporation surface was determined from the corrected readings of the dry- and wet-bulb thermometers using the formula:

$$h = H - Ab\,(t_c - t_m)$$

where $\varphi = \frac{h}{p_H} \times 100$
h = partial pressure of water vapor
t_c = corrected dry-bulb temp.
t_m = corrected wet-bulb temp.
p_H, H = water vapor pressure at full saturation and temp. t_c and t_m
A = Reknagel's psychrometric coefficient
$A = 0.00001\left(65 + \frac{6.15}{v}\right)$
v = air velocity, m./sec.

At the same time the air humidity was determined graphically by the *I-d* diagram (*7*). The Carrier and Lindsay diagrams (*2*) were used for determination of the true evaporation temperature.

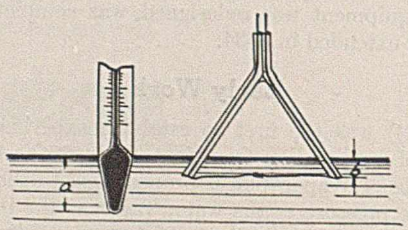

FIGURE 2. COPPER-CONSTANTAN THERMOCOUPLE

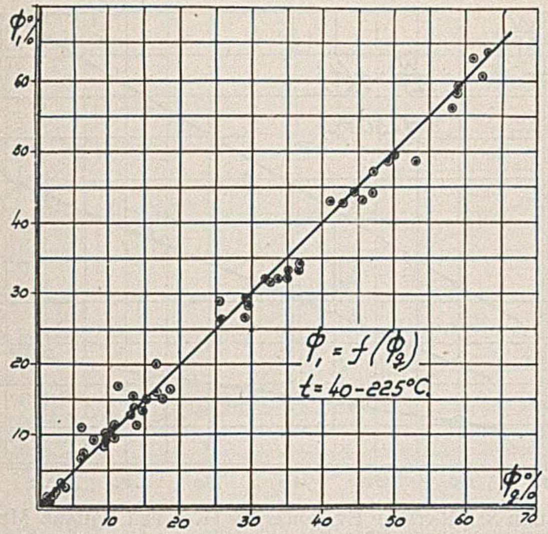

FIGURE 3. RELATIVE HUMIDITY WITH RECKNAGEL'S CORRECTION *vs.* RELATIVE HUMIDITY DETERMINED GRAVIMETRICALLY

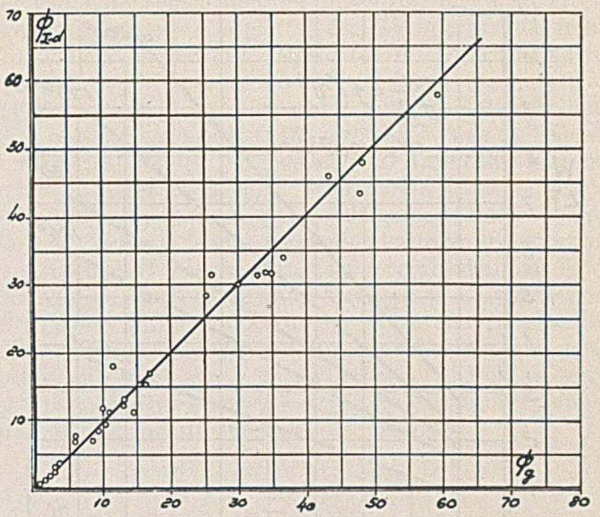

FIGURE 4. RELATIVE HUMIDITY WITH CARRIER AND LINDSAY'S CORRECTION *vs.* RELATIVE HUMIDITY DETERMINED GRAVIMETRICALLY

The humidity was also determined gravimetrically, by aspirating air slowly through two tubes filled with P_2O_5. The aspiration rate was slow enough so that one determination covered about half the test period.

The air velocity in the circular duct was measured by a sharp-edged orifice, inserted nearly in the middle of the lower horizontal section. A length of about eight diameters was passed prior to each turn, and consequently a good equalization of air flow was secured.

The discharge coefficient of the orifice was taken from the work of the Republic Flow Meters Company (*10*). The average air velocity at the evaporation surface was calculated from the air velocity in the circular air duct section.

The temperature of the evaporating water was measured by an accurate mercury thermometer, graduated to 0.1° C. and certified by the P. T. R. A correction for the emergent stem was made as for the wet-bulb thermometer.

The thermometer bulb was immersed in the liquid so that it was just covered with water. Since the thermometer bulb was of relatively large size, the average film temperature must be considered rather than that of the evaporation surface proper. This was checked by the temperature measurement of a very thin film by means of a thermocouple made of two thin copper-constantan wires (Figure 2). No marked or systematic difference was observed.

The test was started only when stable conditions for the entire system were established; for this purpose the ventilation system was run for a considerable period of time at a given temperature, air humidity, and rate; after the air conditions became stable, the observation of the evaporating water temperature began. This became uniform through the entire depth after a certain period of time (sometimes very considerable) under conditions close to those of adiabatic evaporation, whatever the temperature of water in the reservoir. This was considered to be the beginning of the thermal equilibrium between air and evaporating water. After a somewhat higher water level was established in the evaporating vessel, the start of the test was taken as the time when the water level became accurately equal to that shown by the needle. At this instant the meniscus in the inclined glass tube was recorded. Then 25 cc. of distilled water were added by means of a pipet. After the meniscus in the inclined tube came to the initial state as a result of further evaporation, another 25 grams of water were added, the time being recorded in each case. The end of the test was established after the evaporation of 800 to 1000 cc. of water (twenty to forty readings were taken, depending on the evaporation), when the position of the meniscus in the indicating tube coincided with that which existed at the start of the test. At the same time the level of the evaporation surface in respect to the needle was recorded, and, if it did not correspond closely to the meniscus, the test was repeated.

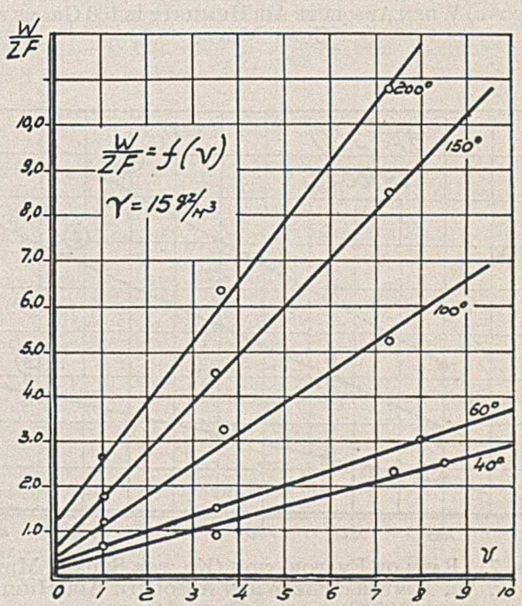

FIGURE 5. RATE OF EVAPORATION (KG. PER SQUARE METER PER HOUR) *vs.* AIR VELOCITY (METERS PER SECOND) WHEN ABSOLUTE AIR HUMIDITY IS 15 GRAMS PER CUBIC METER

The evaporation rate per square meter was calculated from the amount of the water added and the time during which the water was being evaporated.

Experimental Results

About two-hundred experiments were carried out; eighty-eight were successful and were calculated. The time of the test was from 2 to 10 hours. From these experiments, apart from the numerical evaporation rate values, the following conclusions can be drawn:

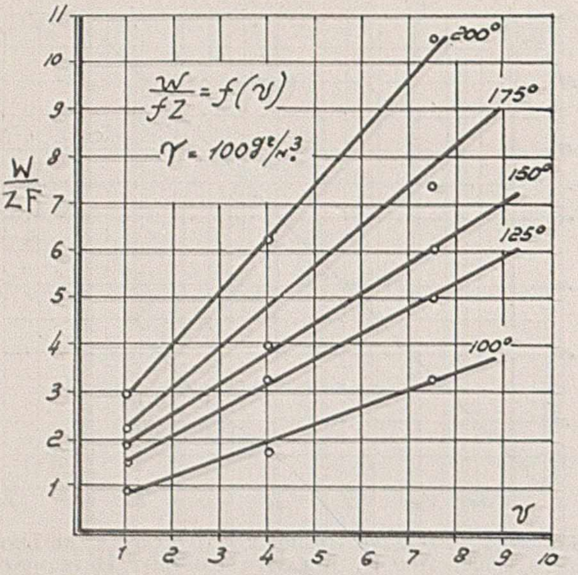

FIGURE 6. RATE OF EVAPORATION (KG. PER SQUARE METER PER HOUR) *vs.* AIR VELOCITY (METERS PER SECOND) WHEN ABSOLUTE AIR HUMIDITY IS 100 GRAMS PER CUBIC METER

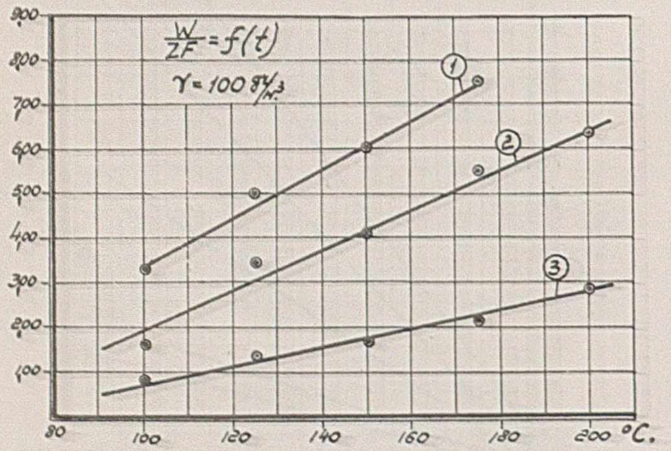

FIGURE 7. RATE OF EVAPORATION (KG. PER SQUARE METER PER HOUR) *vs.* AIR TEMPERATURE WHEN ABSOLUTE AIR HUMIDITY IS 100 GRAMS PER CUBIC METER

(1) $V \cong$ 7.5 meters per second
(2) $V \cong$ 3.9 meters per second
(3) $V \cong$ 1.1 meters per second

1. The evaporation water temperature under equilibrium conditions and in the absence of losses to the surrounding medium is close to that of the wet-bulb thermometer.
2. With a pan 150 mm. deep, the temperature variation at different depths (under equilibrium conditions and with addition of water at the same temperature) is negligible.
3. The maximum air velocity at which fine water particles are not torn away from the edge of the vessel is 8 to 9 meters per second.
4. For all air temperatures studied (40° to 225° C.) the relative air humidity measured by a psychrometer is close to that measured gravimetrically (Figures 3 and 4). In these figures,

φ_1 = relative humidity determined by Recknagel's correction
φ_{I-d} = relative humidity with Carrier and Lindsay's correction (2)
φ_0 = relative humidity determined gravimetrically

Consequently the psychrometer may be used at air temperatures over 100° C., using the same coefficients.

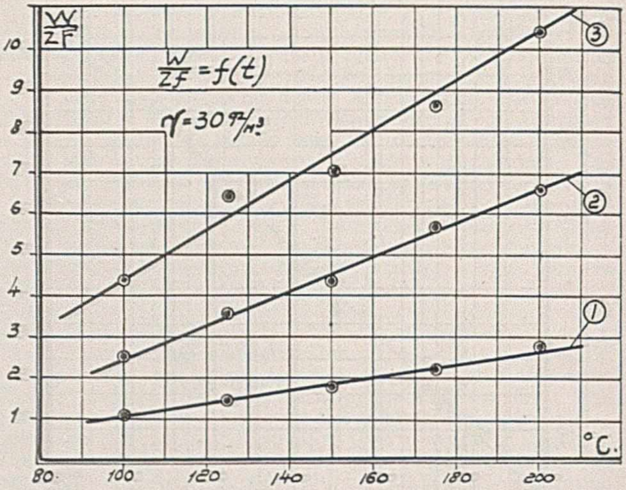

FIGURE 8. RATE OF EVAPORATION (KG. PER SQUARE METER PER HOUR) *vs.* AIR TEMPERATURE WHEN ABSOLUTE AIR HUMIDITY IS 30 GRAMS PER CUBIC METER

(1) $V \cong$ 1.1 meters per second
(2) $V \cong$ 3.9 meters per second
(3) $V \cong$ 7.5 meters per second

In Figures 5, 6, 7, and 8 the relation between the rate of evaporation and air rate and temperature at a constant absolute air humidity, γ, is given. These figures show that a straight-line function may be used as a first approximation. The points seem to be somewhat scattered because of variation of the absolute air humidity with different experiments.

The effect of air temperature and saturation can be correlated by a so-called drying potential—that is, a pressure difference between saturated steam at the temperature of the wet bulb thermometer, H, and the partial pressure of steam, h, of the temperature and saturation of the moving air. Since the dry-bulb (t_c) and wet-bulb (t_m) temperatures were obtained by experiment, the pressure difference can be estimated from the Recknagel formula:

$$H - h = Ab\,(t_c - t_M)$$

where b = barometric pressure
A = psychrometric coefficient depending on air velocity and equal to $0.00001\,\dfrac{(65 + 6.15)}{v}$

Plotting the rate of evaporation against the drying potential (Figure 9), it can be seen that within the limits of the given experiments this relation may be taken as linear; that is,

$$\frac{W}{ZF} = C\,(H - h)$$

Coefficient C is a linear function of air velocity. The most probable equation for this line would be:

$C = 22.0 + 16.8\,v$ g./sq. m./hr./mm. Hg partial pressure difference

where v = av. air velocity in duct, m./sec. (the true air velocity at the evaporation surface will be different)

When estimating the drying potential, $H - h$, according to the $I - d$ diagram with Carrier and Lindsay's correction, a somewhat different value of coefficient C would be obtained. The relation between the rate of evaporation, C_1, and the velocity for this case may be expressed as follows:

$$C_1 = 22.9 + 17.4\,v \text{ g./sq. m./hr./mm. Hg}$$

These equations give nearly the same values for coefficient C. Consequently, the rate of evaporation from free water

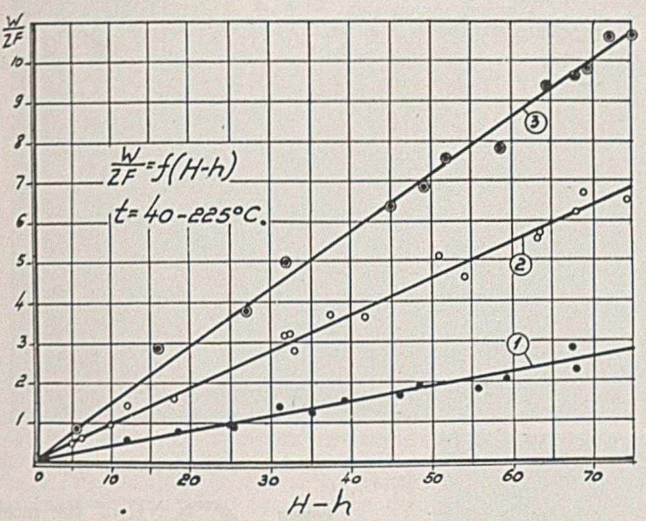

FIGURE 9. RATE OF EVAPORATION (KG. PER SQUARE METER PER HOUR) *vs.* DRYING POTENTIAL RATIO (MM. OF MERCURY)

(1) $V \approx$ 1.1 meters per second
(2) $V \approx$ 3.9 meters per second
(3) $V \approx$ 7.5 meters per second

surfaces for a very wide range of air temperatures (40° to 225° C.) and for air velocities from 1 to 7.5 meters per second, may be considered to be directly proportional to the drying potential in a linear relation to the air velocity.

For comparison of these data with those of previous workers, the writers calculated the values of coefficient C from these experiments, using the same relation for the rate of evaporation:

$$\frac{W}{ZF} = C\,(H - h)$$

The results of these calculations are given in Figure 10; the Carrier and the Coffey and Horn values for coefficient C are plotted on the same diagram for comparison for a perpendicular air flow.

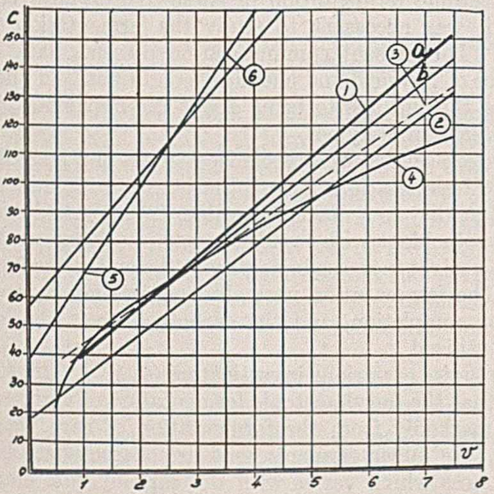

FIGURE 10. COMPARISON OF EVAPORATION COEFFICIENTS

Parallel flow:

(1*a*) Drying Laboratory experiments, $C = 22.9 + 17.4v$
(1*b*) Drying Laboratory experiments, $C = 22.0 + 16.8v$
(2) Carrier experiments, $C = 17.8 + 15.2v$
(3) Himus and Hinchley experiments, $C = 31.0 + 13.5v$
(4) Thiesenhusen experiments, $C = 42.2\sqrt{v}$

Perpendicular flow:

(5) Carrier experiments
(6) Coffey and Horn experiments

The values of coefficients from these experiments are given as two straight lines; *a* is plotted for $H - h$ estimated from the $I - d$ diagram, and *b* is plotted for $H - h$ according to Recknagel.

For the majority of experimental work, the straight-line relation between coefficient C and air velocity was confirmed. The numerical values of coefficient C from the present experiments differ to a small extent from those of other experiments, notwithstanding the wide range of temperatures employed. With air flowing perpendicular to the evaporation surface, coefficient C is twice that for a longitudinal air flow.

The relation found empirically for the rate of evaporation holds true only within limits of temperatures and air velocities studied. Extrapolation beyond the experimental limits must be made with great care. Extrapolation of the air velocity values (particularly for zero velocity) may lead to considerable errors. Himus and Hinchley gave a relation,

$$\frac{W}{ZF} = \left(\frac{H - h}{50}\right)^{1.2} .1000$$

for still air; extrapolation of their formula for evaporation with convection to zero air velocity gives

$$\frac{W}{ZF} = 31.0\,(H - h)$$

When $H - h = 1$, the rates of evaporation calculated from these two formulas will be as 3:1.

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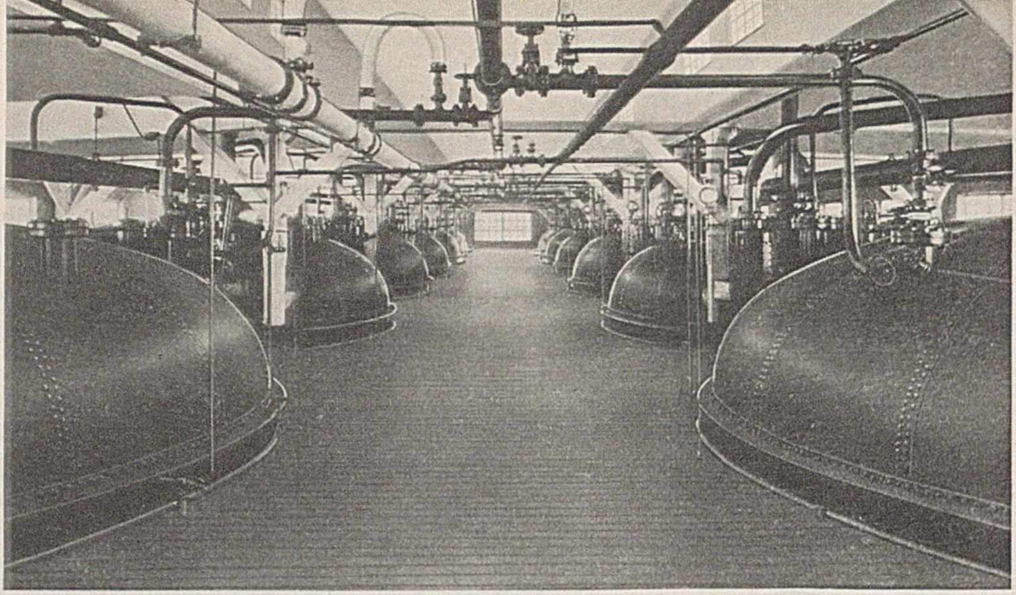

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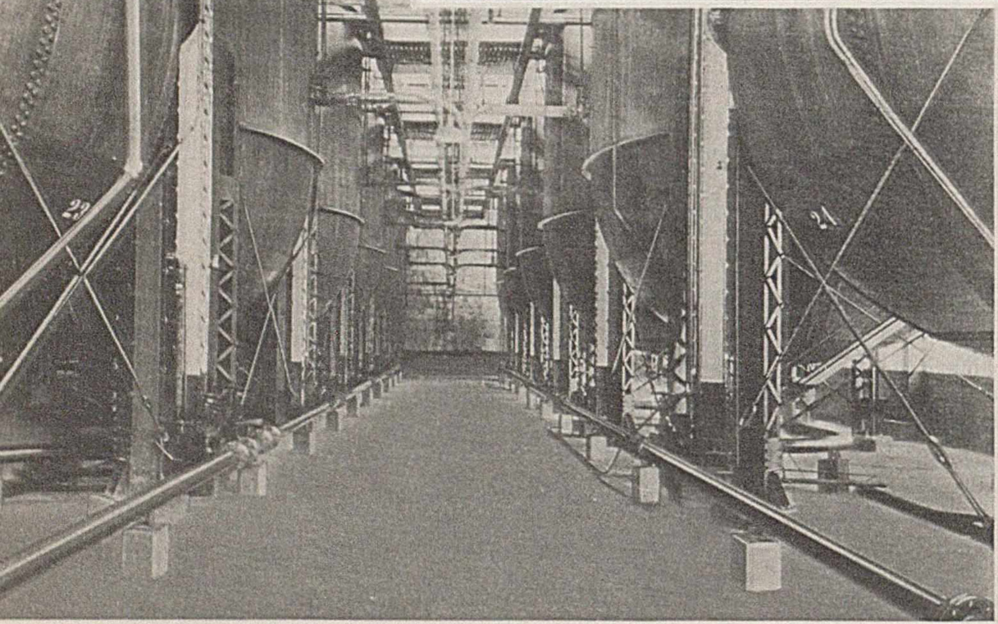

Butyl-Acetonic Fermentation of Xylose and Other Sugars

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ONE of the most important developments in the utilization of agricultural products for the production of industrial chemicals is the butyl-acetonic fermentation of corn. Most of the research has been done on this and other starchy materials. Next to cellulose and lignin, the pentosans, particularly xylan, are probably the most widely distributed organic compounds in nature and constitute a large proportion of the so-called agricultural wastes. It follows that xylose in solution should form a very economical source for chemicals, by fermentative or other processes. In a communication by Bryner, Christensen, and Fulmer (*2*) data are presented on optimum conditions for the production of reducing sugars by the hydrolysis of oat hulls. Before adequate studies of the butyl-acetonic fermentation of these hydrolyzates could be made, it was necessary to study the fermentation of pure xylose. The present communication presents data on the influence of physical and chemical conditions and the treatment of the cultures to bring about the maximum yields of the solvents from xylose.

There are several well-recognized stages in a normal butyl-acetonic fermentation of corn mash: (1) a rapid increase in titrable acidity to a maximum value, (2) a marked decline in acidity coincident with rapid increase in solvent production, and (3) a slight increase in acidity at the end of the fermentation. The fermentation normally requires not more than 3 days for completion, and the carbohydrate is almost completely utilized.

The studies of various investigators (*6, 12, 13, 15, 17*) have shown that the butyl-acetonic fermentation of various sugars differs markedly from the fermentation of corn mash. In general, the sugar fermentations are characterized by their sluggishness which varies with the carbohydrate employed. Sugar fermentations exhibit slower rise in acidity to the maximum value which may be higher or lower than that for corn mash, depending upon the sugar; the decline is slower and in some cases does not occur at all, whereas the final acidity is always relatively high. The fermentations are slower than in corn mash, a week or longer frequently being required. Utilization of carbohydrate is rather poor and the yields, based on total substrate, are lower although yields based on actual carbohydrate consumed are about the same as for corn mash. The fermentation of xylose, of all the readily available carbohydrates, is most sluggish.

Methods

The original culture was isolated in 1931 from a sample of wheat and corresponds in all its characteristics with the organism described by McCoy, Fred, Hastings, and Peterson (*8*) and by Weyer and Rettger (*19*) as *Clostridium acetobutylicum*. This particular culture was selected because it fermented sugars somewhat better than the others tested:

The organism was stored as a spore culture on soil and handled in the customary manner. Inoculation was made from the spore culture into fresh sterile tubes of 6 per cent corn mash which were "heat-shocked" for 2 minutes in a boiling water bath, cooled, and incubated. Transfers were made each 24 hours into fresh corn mash until used for inoculating the experimental flasks, and the fourth to the sixth active transfer from the original spore culture was used to produce the desired fermentation. Inoculations of 2 cc. of culture per 100 cc. of medium were employed, and all fermentations were incubated at 37.5° C. The stock medium for cultures and controls was a 6 per cent sterile corn mash. Unless otherwise stated, sugar fermentations were carried out in semi-synthetic media which contained, in addition to the carbohydrate, 1.0 gram of corn-gluten meal and 0.25 gram of dipotassium phosphate per 100 cc., with 300 cc. of medium being used in each 500-cc. Erlenmeyer flask.

Total acidity is expressed in terms of cubic centimeters of 0.10 *N* sodium hydroxide required to neutralize 10 cc. of the medium with phenolphthalein as indicator. Solvents were determined according to the methods of Christensen and Fulmer (*3*). Sugars were determined by the Marsh and Joslyn modification (*9*) of the Shaffer and Hartmann method (*14*); the factors given by Stiles, Peterson, and Fred (*16*) were used in the calculation of results for the sugars not included in the tables of Munson and Walker (*10*). Sucrose and starch were hydrolyzed by the official methods of the Association of Official Agricultural Chemists (*1*) before titration. All the values given are the averages for duplicate or triplicate determinations.

Solvent yields are expressed in terms of the dextrose equivalent of total carbohydrate in the medium. For example, if 5 grams of solvents were obtained from a medium containing a total of 20 grams of anhydrous dextrose, the yield was 25 per cent. For sucrose ($C_{12}H_{22}O_{11}$) the dextrose equivalent is (2 × 180/342 =) 1.082. The values for starch and xylose are, respectively, 1.111 and 1.000. This method permits the direct comparison of the various carbohydrates on the basis of equal carbon content.

Action of Butyl Organism on Carbohydrates in Presence of Corn Meal

Experiments were undertaken to determine the minimum amounts of corn meal required to furnish adequate nutrients for the fermentation of several carbohydrates. In each case the amount of carbohydrate added was equivalent to that of the corn meal replaced. The results are given in Table I.

The data show that, whereas starch can be used to replace 90 per cent of the corn meal and glucose and sucrose can be used to replace as much as 80 per cent of the corn meal, more than 40 per cent replacement by xylose results in diminished yields of solvents. Less corn meal can be replaced by crude xylose than by recrystallized xylose without lowering the yield. With the exception of xylose, 1.0 to 1.5 grams of corn meal per 100 cc. supply sufficient nutrients for the fermentation of mashes containing 6 per cent carbohydrate.

Table I. Fermentation of Carbohydrate–Corn Meal Mixtures

Corn Meal Replaced, %	Total Solvent Yield, Weight % of Dextrose Equivalent Starch	Dextrose	Sucrose	Xylose[a]	Xylose[b]
0	24.46	27.47	27.48	27.57	28.60
10	...	27.49	27.15	...	...
20	24.72	27.49	27.64	27.59	28.15
30	...	27.81	28.31	...	...
40	24.21	27.38	28.46	27.52	27.21
50	...	28.01	27.47	...	26.09
60	25.49	27.80	27.98	24.77	24.21
70	24.45	...	...	21.94	6.53
80	24.88	24.22	29.45	15.18	...
90	23.86	...	...	2.62	...
100	11.98	3.74	4.23	...	...

[a] Recrystallized xylose.
[b] Crude xylose from Bureau of Standards plant at Anniston, Ala.

Effect of Medium Composition and Environmental Factors on Yield of Solvents from Xylose

Since the amount of corn meal which can be replaced directly by xylose is relatively small, attempts were made to adjust the composition of the medium and to alter environmental factors in order to improve the utilization of xylose by the butyl organism. It was found that relatively little improvement was obtained through varying the kind and amount of nitrogenous nutrients and salts, or by changing factors such as surface-volume ratio, length of incubation, and number of transfers.

Effect of Nitrogen Source. For sugar fermentations in the absence of corn mash, nutrients must be added. Peptone, tankage, corn-gluten meal, casein, steep water, and ammonium chloride were added separately in series of concentrations to a medium containing, per 100 cc., 6.25 grams of pure xylose, 0.2 gram of dipotassium phosphate, and 0.5 gram of pulped filter paper. The filter paper was added to aid in maintaining anaërobic conditions, a procedure used by the investigators (*6, 12, 13, 15, 17,*) who have previously carried out butyl fermentations of sugars; but during subsequent investigations it was found that the filter paper is of no advantage if the medium is cooled immediately following sterilization and inoculated at once. The ammonium chloride and steep water gave the poorest results. The highest yields were obtained with corn-gluten meal.

In order to determine the optimum amount of the corn-gluten meal, two series of fermentations were run. In one series xylose was used and in the second series dextrose. The results are given in Table II.

For dextrose, the maximum yields are obtained with 0.5 to 1.00 per cent of the gluten; the adverse effect of larger amounts may have been due to an unfavorable pH resulting from the buffering value. For xylose the optimum is at about 2.0 per cent, but the yield does not differ greatly between 1.25 and 2.75 per cent.

A procedure is described by which the ability of the butyl organism to ferment sugars is markedly increased. The improvement is especially striking with xylose. Final yields and ratios of solvents obtained by the action of the derived culture on sugars in the semi-synthetic medium are practically the same as on corn mash. The xylose fermentation differs from that of the other sugars studied in that, during the course of the fermentation, the proportion of butyl alcohol increases, that of acetone is practically constant, and that of ethyl alcohol decreases until the ratio is normal at 60:30:10 at the end of the fermentation.

The following salts were added separately in varying concentrations to the corn-gluten-xylose medium: dipotassium hydrogen phosphate, manganese sulfate, sodium chloride, magnesium sulfate, and ferrous sulfate. Of these salts only the dipotassium hydrogen phosphate showed any effect upon the solvent yield, and the effect of this salt was small.

TABLE II. EFFECT OF CONCENTRATION OF CORN-GLUTEN MEAL UPON YIELD OF SOLVENTS FROM XYLOSE AND DEXTROSE

Corn-Gluten Meal	Xylose		Dextrose	
	Time	Total solvents[a]	Time	Total solvents[a]
G./100 cc.	*Days*		*Days*	
0	10	1.0	3	2.5
0.25	10	1.0	6	26.8
0.50	10	6.1	3	30.8
0.75	8	21.7	3	30.5
1.00	8	24.5	3	29.1
1.25	5	26.2	3	28.4
1.50	5	27.4	3	28.3
1.75	5	28.7	4	28.2
2.00	5	29.0	4	27.5
2.25	..	...	4	26.4
2.50	6	27.2	.	..
2.75	8	26.0	4	6.7
3.00	..	...	4	6.4

[a] Weight per cent of dextrose equivalent.

INFLUENCE OF SURFACE-VOLUME RATIO. Table III gives data on the influence of surface-volume ratio upon the yield of solvents from corn mash, dextrose, and xylose. There is the same relative increase in solvents with decrease in surface-volume ratio.

INFLUENCE OF PROLONGED INCUBATION. It has been found in industrial practice with corn mash that, after active fermentation has ceased, the solvents decrease in amount and the acidity increases. The same phenomenon was observed for the fermentation of xylose in the semi-synthetic medium. The yield reached a maximum of 25.9 per cent at 6 days and dropped to a value of 21.5 per cent at the thirteenth day.

INFLUENCE OF NUMBER OF TRANSFERS FROM STOCK SPORE CULTURE. In the usual practice, after inoculation of the corn mash from a spore culture, transfers are made from the active cultures into new medium each 24 hours, and the fourth, fifth, or sixth transfer is used to produce the desired butyl fermentation. A series of flasks containing xylose in the semi-synthetic medium was inoculated on successive days from an active culture in corn mash carried by repeated daily transfers as already outlined. The best yields of solvents were obtained when the fermentation was from the fourth to the seventh transfer. The eighth and ninth transfers gave very slow fermentations with reduced yields of solvents; the medium became very slimy and viscous.

Development of Culture of Butyl Organism to Improve Its Utilization of Sugars

Acclimatization of cultures of various organisms to grow in or to ferment, media containing substances which are unfavorable or carbohydrates which are poorly utilized has been frequently reported. For instance, Fulmer (*4*) acclimatized yeast to grow in the presence of ammonium fluoride. In general it has been found that repeated subculturing in the presence of an unfavorable carbohydrate, often under special conditions, results in increased ability to utilize that particular carbohydrate. For example, Patwardhan (*11*) found that *Bacillus acetoethylicus*, which did not grow on media containing high concentrations of pentoses alone, could be acclimatized to 7 per cent pentose concentration by using diminishing quantities of hexoses with increasing concentrations of pentoses until abundant growth of the organism and vigorous fermentation were obtained in a medium containing no hexose.

TABLE III. VARIATION OF YIELDS OF TOTAL SOLVENTS WITH CHANGE IN SURFACE-VOLUME RATIO OF FERMENTATIONS

Flask Size	Vol. of Medium	Surface	Surface-Volume Ratio[a]	Yield, Per Cent of Dextrose Equivalent		
				Corn	Dextrose	Xylose
Cc.	*Cc.*	*Sq. cm.*				
150	100	22.5	0.225	20.59	20.40	19.58
500	300	50	0.167	24.66	24.42	22.50
1000	750	62	0.083	27.10	28.79	24.52
2000	1500	80	0.053	28.66	30.02	25.90
4000	3000	110	0.037	30.24	31.40	27.00

[a] Ratio of surface (sq. cm.) to volume (cc.).

It is well known that yields of solvents from butyl-acetonic fermentations can be increased by proper treatment of the cultures. Probably Grimbert (*5*) was the first to report the modification of a butyl-alcohol-producing culture by means of

INTERIOR OF A STILL TOWER

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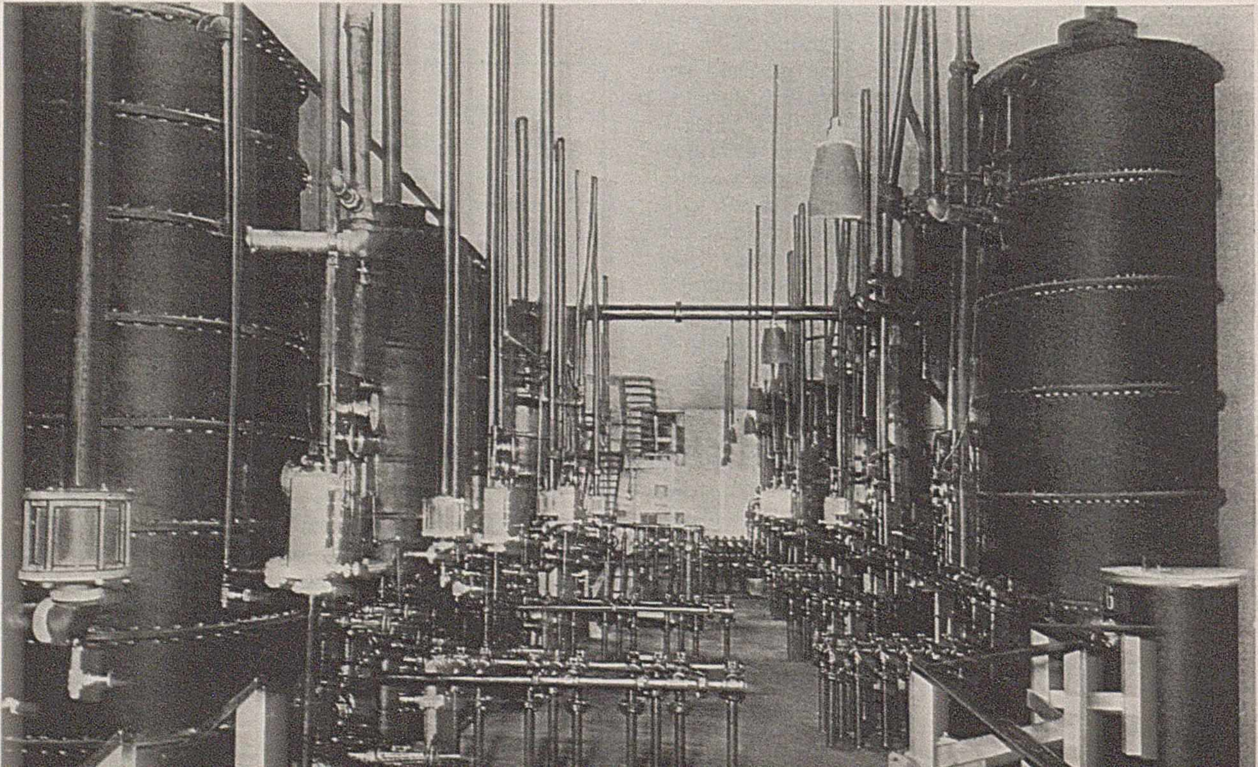

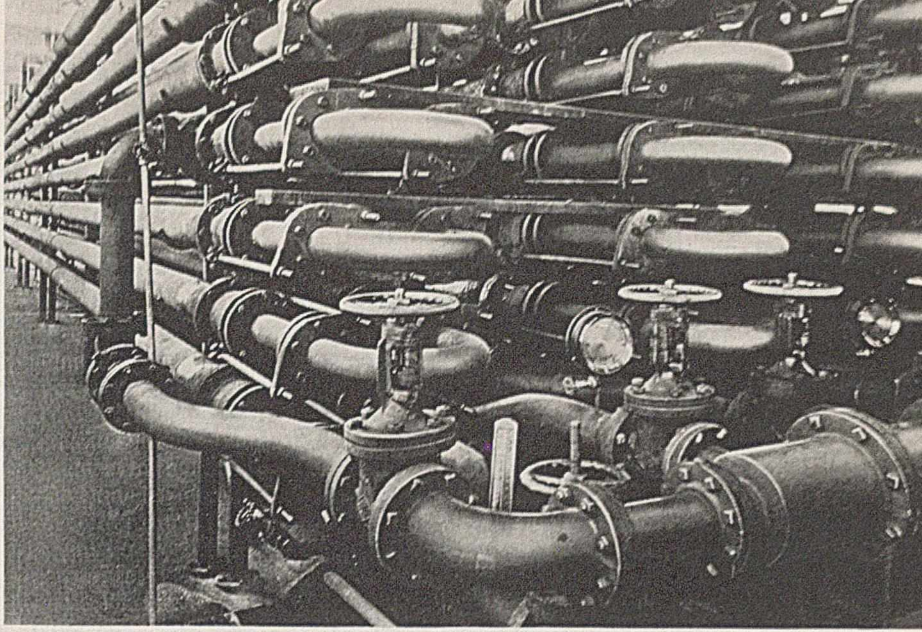

COOLERS

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repeated subculturing. Poorly fermenting cultures can be greatly improved by repeatedly growing, sporulating, and heat-shocking or pasteurizing. Weizmann (*18*) states in his patent that such treatment should be repeated one hundred to one hundred and fifty times. Legg's patent (*7*) for improving sluggish cultures makes use of this repeated subcultivating and heat-shocking. Weyer and Rettger (*19*) state that the almost continued culturing, with periodic pasteurization after complete sporulation, during a period of 2 years, resulted in an average increase in solvent production of over 100 per cent for four strains of the butyl organism. The customary method is to inoculate corn mash in long fermentation tubes from a spore culture, heat-shocking the inoculated tubes before incubating, and then subculturing at daily intervals for four or five transfers. The completely fermented material of the last transfer is allowed to stand for several days at room temperature for sporulation. New tubes of corn mash are then inoculated from this spore culture, and the cycle is repeated.

Since repeated subculturing, sporulation, and heat-shocking in corn mash so markedly improve the fermenting powers of butyl cultures on corn mash, it seemed logical to believe that such treatment in sugar media might improve sugar fermentations. Efforts to sporulate the culture in sugar media in the customary fermentation tubes by the usual method resulted in failure. However, it was discovered that, when the fermented sugar medium is spread out in a thin layer in a relatively large sterile flask, sporulation takes place readily. The fermentations were carried out in fermentation tubes containing sugar media in the usual manner but, instead of setting the tubes aside for sporulation after fermentation was completed, the freshly fermented sugar medium (about 20 cc.) was poured, with care against contamination, from each tube into a sterile 300-cc. Erlenmeyer flask which was again closed with a sterile cotton plug to allow free access of air. After standing for 6 days, inoculation was made from these flasks into corn mash and semi-synthetic dextrose medium. The fermentations started promptly after the customary heat-shocking.

To determine whether repeated transfer, sporulation, and heat-shocking in sugar media would produce cultures which were more useful in the fermentation of sugars than the original butyl culture, inoculation from the above-mentioned spore culture in sugar medium was made into semi-synthetic xylose and semi-synthetic dextrose media. The tubes were heat-shocked for 2 minutes, cooled, and incubated. Growth was vigorous in the dextrose medium, but none occurred in the xylose medium. From the dextrose culture, transfers were made into dextrose medium each 24 hours until four transfers had been made. After completion of fermentation, the fourth transfer was poured into a sterile Erlenmeyer flask and allowed to sporulate for 6 days. Inoculation was then made from the flask into fresh dextrose medium, the tubes were heat-shocked, and the cycle was repeated. After the sixth cycle, instead of pouring the fourth transfer into a flask, the culture in glucose was poured upon sterile soil and dried in the incubator under sterile conditions. This culture, carried through the six cycles on glucose medium, while it fermented corn mash normally with about the same speed and gave about the same yields of solvents as the original culture, fermented all the sugars which were tested much more rapidly and with better solvent yields. In Table IV are presented data on the fermentation of several carbohydrates by the original culture and by the culture derived from it. The times required for completing the fermentations of the various substrates are given, as well as the yields of total solvents. The fermentations were carried out with 350 cc. of medium in 500-cc. Erlenmeyer flasks. The carbohydrates were present in concentrations equivalent to 7 per cent corn mash. Fermentation was judged completed when gassing ceased, and the fermented liquid was then distilled immediately and analyzed for total solvents.

TABLE IV. FERMENTATION OF CARBOHYDRATES BY TWO RELATED CULTURES

	Original Culture		Derived Culture	
	Time of fermentation, hours	Yield of total solvents, per cent of dextrose equivalent	Time of fermentation, hours	Yield of total solvents, per cent of dextrose equivalent
Corn mash	78	30.24	81	30.70
Dextrose	128	28.82	107	30.03
Levulose	88	29.91	65	32.03
Maltose	83	28.97	65	30.96
Xylose	289	27.00	136	29.70

The length of time required for completion of a fermentation of xylose by the derived culture was only 47 per cent of that required with the original culture, whereas the yield of solvents increased 10 per cent. For dextrose, maltose, and levulose fermentations, respectively, the times required for completion of the fermentations with the derived culture were 83.6, 78.4, and 74.9 per cent of that required with the original culture, and yields of solvents increased 4.20, 6.88, and 7.09 per cent. This new treatment of the culture produces a remarkable improvement in sugar utilization, especially with xylose.

Similar treatment of the original culture was tried with other sugars. No success attended efforts to start a spore culture in xylose medium, but spore cultures started readily in media containing sucrose, levulose, and maltose. When xylose medium was inoculated with an actively growing culture, it was fermented although more slowly than the other sugars mentioned; transfers could be made from tube to tube of xylose medium, and sporulation could be brought about by pouring into flasks in shallow layers or by pouring upon sterile soil and drying, as with other sugars. Successive growth, transfer, and sporulation in media containing various sugars produced, in all cases, cultures which gave increased yields of the solvents and increased rates of utilization of the sugar. Transfer, sporulation, and heat-shocking in a medium containing a specific sugar did not give the culture an ability to utilize this sugar more readily than the others. Fermentation of corn mash continued normal after the treatment.

TABLE V. SOLVENT RATIOS FOR SEVERAL CARBOHYDRATES

Time	Per Cent Butyl Alcohol[a]						Per Cent Acetone						Per Cent Ethyl Alcohol					
Hours	St	D	M	L	Su	X	St	D	M	L	Su	X	St	D	M	L	Su	X
0	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
18	65	..	..	..	..	..	22	..	..	..	..	..	13	..	..	..	..	..
24	63	71	76	63	..	..	27	22	24	24	..	..	10	7	..	13	..	..
31	57	64	59	62	..	..	28	26	30	25	..	..	15	10	11	13	..	..
34	60	62	61	69	..	..	26	25	29	25	..	..	14	13	10	6	..	..
40	63	66	61	60	..	29	25	22	25	27	..	25	12	12	14	13	..	46
46	61	63	60	55	73	31	25	23	27	26	26	24	14	14	13	19	1	45
48	..	..	..	..	..	42	..	..	..	..	..	27	..	..	..	..	..	31
55	60	63	55	59	67	40	25	25	27	24	30	28	15	12	18	17	3	32
65	64	60	59	61	65	54	25	25	25	23	28	29	11	14	16	16	7	17
81	62	65	64	61	67	55	25	25	24	24	29	30	13	10	12	15	3	15
100	..	..	..	..	62	54	..	..	..	..	30	34	..	..	..	..	8	15
118	..	..	..	..	58	59	..	..	..	..	31	29	..	..	..	..	11	12
131	62	65	61	58	65	60	25	26	24	25	31	28	13	9	15	17	4	12
168	..	..	..	..	64	60	..	..	..	..	32	30	..	..	..	..	4	10

[a] St = starch, D = dextrose, M = maltose, L = levulose, Su = sucrose, X = xylose.

Yields of Solvents from Carbohydrates

Fermentations of several carbohydrates, starch, dextrose, maltose, levulose, sucrose, and xylose, along with corn mash controls, were carried out in the semi-synthetic media, using the derived culture; periodic analyses were made during the continuation of the fermentations. There was considerable difference in the rate of utilization of the various carbohydrates; starch and levulose were most rapidly fermented, sucrose and xylose most slowly. However, the final total yields of solvents were very similar on the basis of dextrose equivalent. This means that the yield per mol of xylose fermented is five-sixths that for glucose.

Previous investigators have noted that the yields of the three major neutral products in normal butyl-acetonic fermentations occur in the approximate ratio 60 per cent butyl alcohol, 30 per cent acetone, and 10 per cent ethyl alcohol. The exact ratio varies somewhat with the substrate and conditions of the fermentation but, for all substrates studied during the present investigation, the final ratios of the three solvents at the completion of fermentation do not deviate greatly from the above ratio. Data are presented in Table V which show that this ratio of solvents holds practically constant throughout the fermentations in the case of carbohydrates containing 6 carbon atoms per molecule, or capable of hydrolysis to yield such sugars, except that the percentage of butyl alcohol may be a little higher at the beginning of the fermentation, and ethyl alcohol a little lower, but that for xylose this ratio of solvents is not constant. As the fermentation of xylose proceeds, the proportion of butyl alcohol markedly increases, that of acetone is practically constant, and the percentage of ethyl alcohol markedly decreases. This variation is from the ratio of 29:25:46 at the beginning of the fermentation to the normal ratio of 60:30:10 after about 118 hours.

Conclusions

1. Up to 80 per cent of corn meal may be replaced by dextrose or sucrose without decreasing the yield of solvents. The replacement may be as high as 90 per cent for starch but is not above 40 per cent for xylose. The presence of 1.0 per cent corn-gluten meal furnishes all the required nutrients for the butyl-acetonic fermentation of the various carbohydrates.

2. The butyl organism does not sporulate readily in ordinary culture tubes. After fermentation has been completed in the culture tubes, sporulation in sugar media may be brought about readily by transferring the liquid to sterile flasks where it forms a thin layer of liquid, or by drying down the liquid on sterile soil.

3. Successive growth, transfer, sporulation, and heat-shocking in semi-synthetic sugar media, the cycle being repeated several times, greatly improves a butyl culture for use in sugar fermentations, with better yields of solvents in sugar media. The effect on xylose fermentations is especially marked, the fermentations being carried through in less than half the time required with the untreated culture, and with 10 per cent better yields.

4. The carbohydrates differ in rate of fermentation but the final total solvent yields are very similar on the basis of the dextrose equivalent. The xylose fermentation differs from that of the other carbohydrates in that, as the fermentation progresses, the proportion of butyl alcohol markedly increases, that of acetone remains practically constant, and that of ethyl alcohol decreases. The final solvent ratio is normal.

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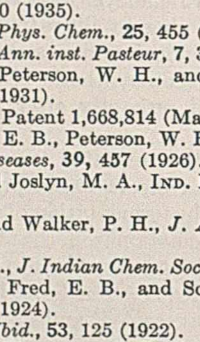

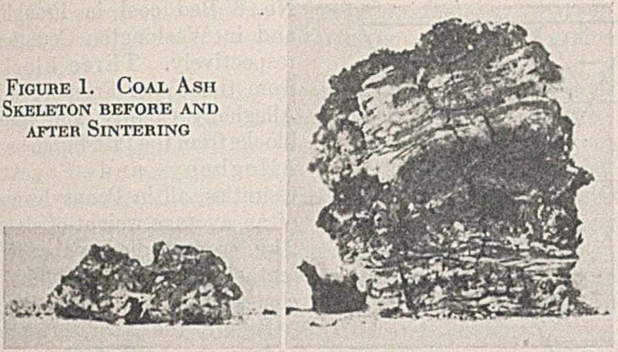

FIGURE 1. COAL ASH SKELETON BEFORE AND AFTER SINTERING

Coal Ash and Coal Mineral Matter

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Examination of numerous coal ash analyses indicates that an average of over 95 per cent of coal ash is composed of the four oxides: alumina, silica, lime, and ferric oxide on a sulfur-trioxide-free basis. Petrographic examination of the separable mineral matter from Illinois and Western Pennsylvania coals shows that it is composed of over 95 per cent detrital clay, kaolinite, calcite, and pyrite, with other minerals unimportant. Ash-softening temperatures are functions of compositions in terms of the four oxides mentioned, as shown by results of tests on oxide mixtures. Coal ash compositions occupy a limited part of the quaternary diagram. Of the four faces of the quaternary tetrahedron, one ternary face is known. On this face, ash-cone softening temperatures are related to liquidus isotherms. Methods for estimating ash-softening temperatures are useful if ash analyses are available. A rapid ash analysis method would be valuable. Clinker formation is affected by mode of occurrence and distribution of the most fusible component in ash. The accelerating influence of pyrites on clinkering is due to the iron oxides formed during its combustion. Iron sulfide has a sharp melting point and gives rise to a very fluid liquid which has no tendency to bind loose particles of coal ash together and is immiscible with fused ash.

THE behavior of a coal ash during the combustion of a coal in a furnace is important in the evaluation of that coal as fuel. Our knowledge of the behavior of coal ash is still largely empirical, in spite of recent progress, and, until more is known about the manner of occurrence and distribution of the ash-forming mineral matter in the coal and the relationships between ash composition and thermal behaviors, attempts to improve the characteristics of coal ashes will have to remain on an empirical cut-and-try basis. There is a growing trend toward extensive preparation of coal. It would be highly desirable if the ash characteristics of certain coals could be greatly improved by preparation. It is with that in mind that the studies here reported were undertaken. Among the more important phases of the coal ash problem are the relationships between ash composition and ash-softening temperature, between ash-softening temperature and tendency to clinker, and between the distribution and occurrence of mineral matter in the coal and the tendency of the ash to form clinkers. This report is to be considered as a preliminary survey to a more detailed study of certain phases of the problem.

Coal Mineral Matter

Examination of numerous coal ash analyses, calculated to a sulfur-trioxide-free basis indicates that over 95 per cent of coal ash is composed of alumina, silica, ferric oxide, lime, and magnesia. The magnesia content is frequently negligible. The remaining 5 per cent includes such items as sodium oxide, potassium oxide, phosphorus pentoxide, chlorine, titanium oxide, together with analytical errors. The values for the items making up the 5 per cent become even less important when converted to the basis of the original mineral matter, because the original mineral matter includes water of hydration of the clay minerals, carbon dioxide, pyritic sulfur combined with iron in place of oxygen. It is, therefore, permissible to consider coal ash as a system comprised of alumina, silica, lime, magnesia, and iron oxides. The ash analyses were converted to a sulfur-trioxide-free basis in order to make them comparable since sulfur trioxide appears, as will be shown later, to have no influence upon the softening temperature of the ash. As shown by the negligible sulfate sulfur content of the coal, the sulfur trioxide in the ash is not a component of a definite sulfate mineral in the coal (*15*). The amount of sulfur trioxide retained in ash may vary widely, depending upon conditions existing during the combustion of the coal.

The number of minerals which might have been present in the coal to give ash compositions as found is very large, and some authors have presented extended lists of the minerals which they state occur in coal. These lists are based upon assumptions as to "probable" minerals from the chemical analyses or upon qualitative mineralogical examinations. A quantitative mineralogical study of an Illinois coal has shown that pyrite, calcite, silica, and the clay minerals (mainly

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[1] Responsible for the portion of the paper relating to the character and constitution of coal mineral matter. Now associated with the Bell & Zoller Coal Co., Chicago, Ill.

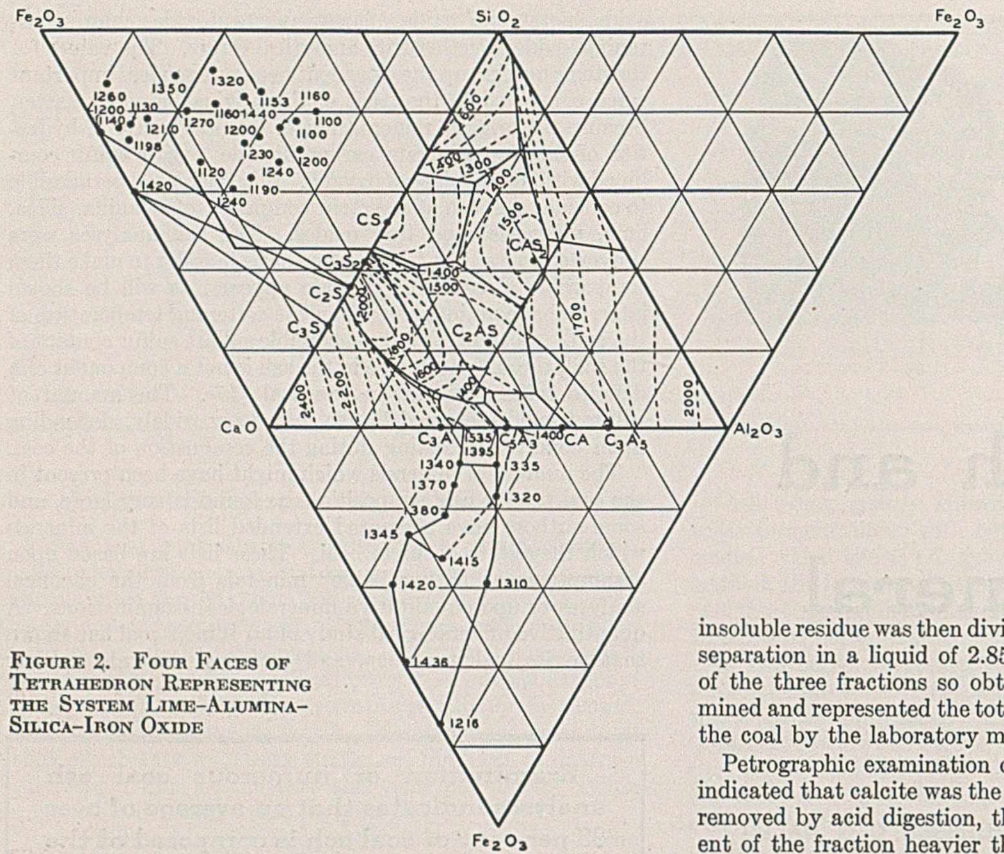

FIGURE 2. FOUR FACES OF TETRAHEDRON REPRESENTING THE SYSTEM LIME-ALUMINA-SILICA-IRON OXIDE

kaolinite) make up over 95 per cent of the mineral matter in the coal (*3*, *4*). A number of other minerals are found in the Illinois coals under investigation, but they occur in such small quantities that individually they are negligible in effect. They are detrital minerals brought in by wind and water from areas outside the coal-swamp basin. There is, as might be expected, a striking accord between the prevailing mineralogical composition of the coal mineral matter and the chemical make-up of coal ash. Detailed studies of the mineral matter in the natural benches of the Illinois coal studied have established the vertical range in mineral matter abundance and composition throughout the entire thickness of the bed.

Whether the results obtained from the mineralogical studies of Illinois coals are applicable to other coals is not definitely known, since no quantitative mineralogical investigations of other coals are available.

Mineralogical studies of seven samples of coal and three samples of washery refuse, all of unstated origin, have recently been reported by Gauger, Barrett, and Williams (*9*). The published results of their investigations do not include quantitative data relative to the occurrence of the various determined minerals. In calculating ash analyses to mineral matter values, however, they assume muscovite to be an important mineral in coal. In one case their calculations involve the assumption that over one-fourth of the mineral matter in coal is muscovite. Although muscovite has been identified in Illinois coal, it is one of the detrital minerals which occur in very small amounts. The question of the similarity of the mineral matter in Pennsylvania and Illinois coals was thus raised. To answer this question, a rapid quantitative mineralogical examination of the separable mineral matter in six bituminous coals from Pennsylvania was conducted. The results of this investigation were entirely in accord with the results so far obtained for Illinois coals.

The Illinois coal so far quantitatively studied consists of two columns, each representing the mined thickness of Herrin No. 6 Bed coal in Franklin and in Washington Counties, respectively. Three blocks from the Upper Freeport bed, Allegheny County, and three blocks from the Pittsburgh bed, Allegheny and Fayette Counties, all in Pennsylvania, of an average weight of about 2 kg., were studied by the same methods used for the Illinois coals.

Briefly, the laboratory procedure consisted of separating the mineral matter from finely crushed coal in a liquid of 1.70 specific gravity. After preliminary microscopic inspection of the mineral matter so separated, the mineral fraction was digested in dilute hydrochloric acid to remove the acid-soluble minerals. The acid-insoluble residue was then divided into two fractions by gravity separation in a liquid of 2.85 specific gravity. The weights of the three fractions so obtained were each carefully determined and represented the total mineral matter separable from the coal by the laboratory methods employed.

Petrographic examination of the various mineral fractions indicated that calcite was the chief, and perhaps only, mineral removed by acid digestion, that pyrite was the chief constituent of the fraction heavier than 2.85 specific gravity, and that clay, partly in the form of kaolinite, formed the bulk of the mineral fraction lighter than 2.85 specific gravity. The clay material in the latter fraction consisted of two forms, a detrital variety which was deposited contemporaneously with the peat and which has not been specifically identified, and a well-established kaolinite variety (*2*) which occurs in desiccation cracks and in fusain cavities throughout the coal. The proportions of these two varieties in the mineral fraction lighter than 2.85 specific gravity were determined by visual estimation and by microscopic counts. Detrital minerals other than clay were found in both of the acid-soluble mineral fractions but were invariably minor in amount. The following minerals were identified: quartz, feldspar, garnet, hornblende, apatite, zircon, epidote, staurolite, muscovite, tourmaline, andalusite, and chloritic material. Except for quartz and feldspar, these minerals were irregular in occurrence; there were usually only 2 or 3 grains of the mineral in the entire column. Because of the scarcity of detrital minerals other than clay, they were disregarded in establishing the quantitative composition of the mineral matter. The total mineral matter, accordingly, was considered as consisting only of calcite, pyrite, detrital clay, and kaolinite.

The separable mineral matter of each of the six coals from Pennsylvania was divided into three mineral fractions by the procedure used in the study of the Illinois coal. Careful petrographic study of each fraction indicated that they consisted primarily of the same minerals found in the Illinois coals. Calcite, pyrite, detrital clay, and kaolinite, accordingly, formed over 99 per cent of the total separable mineral matter and were considered quantitatively as composing all of the mineral matter. One exception to such composition was discovered; one of the coals contained a small amount of anhydrite, amounting to approximately 3 per cent of the total mineral matter. The detrital minerals other than clay which occurred in the mineral separates consisted of quartz, feldspar, epidote, hornblende, topaz, titanite, apatite, muscovite, staurolite, and zircon. Quartz was the only detrital mineral of which a moderate number of grains was found in the specimens studied; of the other detrital minerals, only 1 or 2 grains were found.

The data relative to mineral matter abundance and composition in the coals from Illinois and Pennsylvania are summarized in Table I. In the first two columns the maximum and minimum amount of the mineral matter in the coal, and of the calcite, pyrite, detrital clay, and kaolinite in the mineral matter in any one bench of the two coal columns studied are indicated. In addition, the average amount of the mineral matter and each mineral component for the entire thickness of the coal are given. The third column gives similar amounts of the mineral matter and the mineral components separated from the six Pennsylvania coals. Since each block came from a different mine, no average values were computed.

Proximate analyses of face samples corresponding to the two columnar samples of Illinois and ash contents of the blocks of Pennsylvania coals are presented in Table II. In taking the face samples, the "blue band" and other parts of the seam not normally included with the mined coal were excluded.

Although the separable mineral matter of the coals from Pennsylvania contains the same mineral components as that in Illinois, certain differences exist. It is evident that the separable mineral matter in the eastern coals, so far as represented by the small number studied, is considerably less than that in Illinois. Calcite in the coals from Pennsylvania is much less concentrated than in Illinois. Pyrite occurs in nearly as great concentration in Pennsylvania coals as in Illinois and, moreover, forms a larger proportion of the mineral matter than in many benches of Illinois coals. Its amount in the coal, however, is very small, as evidenced by the low proportion of total mineral matter to the coal. Concentration of detrital clay and kaolinite is approximately similar for both coals, although the kaolinite, like the pyrite, seems to form a larger proportion of the total mineral matter in Pennsylvania than in Illinois. Anhydrite has not been found as yet in Illinois coals.

In view of the limited number of Pennsylvania coals examined, however, and since the full thickness of any one coal bed was not available for detailed study, these differences in concentration are not of comparative value. It is of considerable importance, however, that the composition of the separable mineral matter in six fairly widespread coals from Pennsylvania is found to be essentially the same as that of the mineral matter in Illinois coals. Additional study of coals from both basins would considerably enhance the available information concerning mineral matter in coal.

TABLE I. RESULTS OF PETROGRAPHIC STUDY OF SEPARABLE COAL MINERAL MATTER

Location of coal:	Franklin County, Ill.	Washington County, Ill.	Allegheny and Fayette Counties, Pa.
	%	%	%
Mineral matter in coal:			
Max. in any one bench	7.82	31.08	1.35
Min. in any one bench	0.42	0.39	0.51
Av. in total column	3.91	8.56	...
Calcite in mineral matter:			
Max. in any one bench	67.36	68.28	12.93
Min. in any one bench	1.07	3.01	4.51
Av. in total column	22.67	9.15	...
Pyrite in mineral matter:			
Max. in any one bench	63.75	79.35	59.75
Min. in any one bench	0.21	0.28	16.73
Av. in total column	11.34	15.79	...
Detrital clay in mineral matter:			
Max. in any one bench	79.23	94.38	53.57
Min. in any one bench	...	...	1.89
Av. in total column	42.38	68.89	...
Kaolinite in mineral matter:			
Max. in any one bench	95.20	64.24	66.28
Min. in any one bench	5.05	0.78	11.16
Av. in total column	23.62	6.17	...
Anhydrite:			
Max. in any one bench	...	...	2.50
Min. in any one bench	...	...	...

TABLE II. PROXIMATE ANALYSES OF FACE SAMPLES CORRESPONDING TO COLUMNAR SAMPLES OF ILLINOIS COALS, AND ASH AND SULFUR CONTENTS OF PENNSYLVANIA COALS[a] (MOISTURE-FREE BASIS IN PER CENT)

	Illinois Coals	
	Franklin County	Washington County
Laboratory No.	C-11	C-195
Ash	10.7	13.3
Volatile matter	36.1	41.1
Fixed carbon	53.2	45.6
Total sulfur	1.29	4.27
Sulfate sulfur	0.02	0.47
Pyritic sulfur	0.80	1.56
Organic sulfur	0.47	2.24

	Pennsylvania Coals					
	Upper Freeport Bed			Pittsburgh Bed		
Specimen:	A	B	C	D	E	F
Laboratory No.	C-1134	C-1136	C-1138	C-1140	C-1142	C-1144
Ash	4.3	4.8	2.5	3.2	3.5	13.61
Total S	1.54	0.68	0.96	1.37	1.23	0.94
Analyses after Removal of Separable Mineral Matter						
Laboratory No.	C-1135	C-1137	C-1139	C-1141	C-1143	C-1145
Ash	3.0	4.4	1.6	2.4	3.1	12.4
Total S	0.53	0.52	0.58	1.02	0.92	0.79

[a] For which results of mineral matter study are given in Table I.

It must be borne in mind that these studies are not on the total mineral matter but only on that portion of the mineral matter separable by the laboratory procedure used. However, evidence obtained by analysis of the ash from coal whose separable mineral matter has been removed leads to the conclusion that the non-separable and separable mineral matter are essentially of the same composition (*3*). Moreover, it is unlikely that the non-separable mineral matter contains minerals in any appreciable quantity which are not found in the separable mineral matter. The statement can be made, therefore, with considerable assurance that the minerals comprising the inorganic matter in the coals investigated here are pyrites, calcite, kaolinite, and detrital clay and silica.

Ash-Forming Reactions

The behavior of the pure minerals in ashing is relatively simple. Calcite loses carbon dioxide to form lime, the clay minerals lose water and form intimate mixtures of alumina and silica until relatively high temperatures are reached; silica is chemically unaffected. Pyrite decomposes by evolving sulfur and forming iron sulfide, which oxidizes to form a mixture of iron oxides, with the black oxide, Fe_3O_4, predominating under the usual conditions.

If a piece of coal is slowly burned at a dull red heat, a skeleton of ash is obtained which is very light, fluffy, and very fragile. Inspection shows that the composition of the ash throughout the skeleton is obviously heterogeneous, each small ingredient of the coal having left an ash deposit characteristic of itself. If this very fragile ash skeleton, which in the case of a swelling coal may have several times the volume of the original piece of coal, is placed in a furnace and heated, the mass shrinks and sinters to form a crusty, brittle cinder of considerable strength. Further heating fuses the mass to a glassy clinker (Figure 1). Examination of the sintered cinder reveals that it is still heterogeneous. The mass still contains powdery unsintered material enclosed in a framework of more easily sintered material. Chemical reactions in the solid and liquid state between the oxide components of the ash are of importance at this stage of clinkering. The ash which is first formed under highly reducing conditions is finally subjected to oxidizing conditions at high temperatures. The final reaction products are those conditioned by the preponderantly oxidizing atmosphere in the lower parts of the fuel bed, assuming combustion to take place on an overfeed or traveling grate. For practical purposes only the compounds of iron are affected by the atmosphere.

Coal Ash System

Coal ash compositions occupy but a portion of the four-component system lime, alumina, silica, and the oxides of iron. The maximum and minimum values for the four oxides in coal ashes are as follows:

Oxide	Maximum %	Minimum %	Oxide	Maximum %	Minimum %
SiO_2	70	15	CaO	55	0
Al_2O_3	40	0	Fe_2O_3	60	0

The areas within which coal ash compositions fall on the four faces of a regular tetrahedron used to represent the system graphically are shown in Figure 2. The composition–temperature phase–equilibrium diagrams, as far as they are known, are also shown on the faces. Figure 3 gives photographs of a solid model showing the corresponding volume in which coal ash compositions are contained.

Various ingenious methods have been used to express graphically the relationship between softening temperature and composition in this system. Estep et al. (*8*) plotted softening-temperature isotherms on planes of constant calcium content cut across a triangular prism, the composition at each level being expressed in terms of the remaining three oxides as 100 per cent. They consider compositions with calcium contents of from 0 to 8.5 per cent, their graphs being based upon actual coal ash analyses. Moody and Langan (*10*) present graphs showing initial deformation and softening-temperature isotherms for compositions with a calcium oxide content of 5 per cent. Their values are based upon determinations made on oxide mixtures. A certain amount of success has also been attained in attempts to treat coal ashes as a ternary system on the grounds that calcium and iron oxides are always basic and exert a similar fluxing action upon the silica and alumina. Such treatment has been given the system by Estep et al. (*8*) and by Nicholls and Reid (*11*, *12*).

Unfortunately, insufficient data are available to permit the establishment of softening temperature–composition relationships for those portions of the system in which fall many of the ashes from Illinois coals.

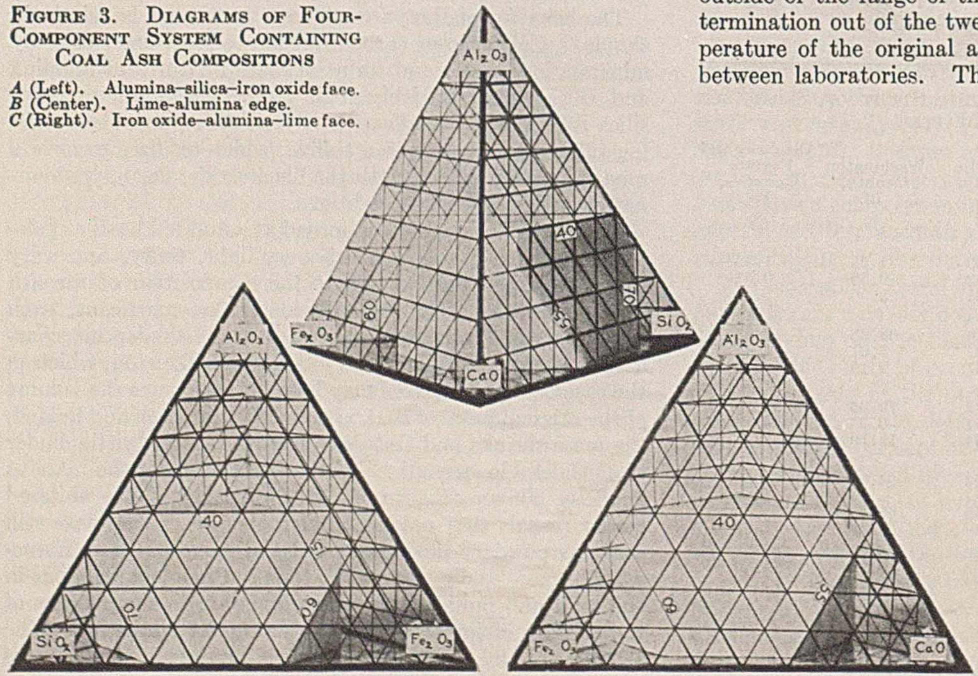

FIGURE 3. DIAGRAMS OF FOUR-COMPONENT SYSTEM CONTAINING COAL ASH COMPOSITIONS

A (Left). Alumina–silica–iron oxide face.
B (Center). Lime-alumina edge.
C (Right). Iron oxide–alumina–lime face.

The analyses of a sufficient number of coal ashes in the proper composition range for the construction of isothermal contours is impractical and one turns to the use of oxide mixtures. When that is done, the validity of ignoring the influence of the oxides other than the four already considered may be questioned, especially since the neglected oxides include such highly fluxing components as the oxides of sodium and potassium. To make sure that different mixtures of the four oxides were respectively equivalent, in fusing properties, to the corresponding natural ashes, the softening temperatures were determined of a number of four-component mixtures corresponding to coal ashes whose compositions and softening temperatures were known. The analyses of the coal ashes, the compositions of the corresponding oxide mixtures, and the respective initial deformation, softening, and fluid temperatures used in this study are given in Table III.

In compounding the synthetic mixtures, the magnesium oxide contents of the coal ashes were calculated to their chemical equivalents of calcium oxide and added to the calcium oxide value on the assumption that lime and magnesia were equivalent in fluxing action and because these two oxides occur in amounts which, while small, are of the same magnitude. The behavior of mixtures F-7 and F-8 indicates that the sulfate content of ash does not materially influence its fusion characteristics. In view of the relatively low decomposition temperatures of the sulfates of the metals found in coal ash, this should not be surprising. With one exception the agreements between the softening temperatures for the ashes and for the corresponding oxide mixtures were satisfactory, more so when it is remembered that the values were determined in different laboratories. According to the A. S. T. M. method (*1*), the allowable difference between duplicate determinations of ash fusion temperature in the same laboratory is 54° F. and between different laboratories 90° F. On this basis, seven out of the twelve determinations of fusion temperature on synthetic mixtures checked the determination of the corresponding ashes within the limits allowable in the same laboratory, an additional three within the limits allowed between laboratories, while one softening temperature fell outside of the range of the equipment used. Only one determination out of the twelve did not check the fusion temperature of the original ash within the tolerance allowable between laboratories. The results on that one sample (F-4, corresponding to sample L) are definitely out of line. The initial deformation and fluid temperatures for the oxide mixture are approximately 200° F. low, and the fusion temperature is almost 300° F. low. Seeking an explanation for these low values, which were substantiated by check determinations on a new mixture, the fusion temperature of the ash was estimated from its composition by the several methods available. The results of these estimates which, in general, substantiate a lower value than that obtained for the original ash are given in Table IV.

From the results of deter-

TABLE III. COMPOSITION AND FUSION TEMPERATURES OF COAL ASHES AND OF CORRESPONDING MIXTURES OF LIME, ALUMINA, SILICA, AND FERRIC OXIDE

	Composition, Per Cent						Ash-Fusion Temp., ° F.		
Sample	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Other	Initial deformation	Softening temp.	Fluid temp.
A[a]	40.4	38.6	5.6	0.5	4.7	10.2	2550	2930	....
F-1[b]	44.9	42.9	7.0	[e]	5.2	0	Out of range of equipment		
D[a]	43.5	27.1	2.1	0.7	20.8	5.8	2180	2440	2580
F-2[b]	45.8	28.7	3.3	[e]	22.0	0	2365	2410	2624
G[a]	41.2	15.9	9.4	0.4	23.1	10.0	1960	2070	2290
F-3[b]	45.7	17.6	11.0	[e]	25.6	0	1913	1999	2258
L[a]	53.5	30.4	0.9	1.0	9.4	4.8	2630	2800	2850
F-4[b]	56.0	31.8	2.4	[e]	9.8	0	2424	2517	2651
N[a]	55.5	22.7	2.1	1.3	12.7	5.7	2110	2280	2460
F-5[b]	58.5	23.9	4.1	[e]	13.4	0	2260	2316	Out of range
O[a]	54.9	26.3	0.5	0.6	12.0	5.7	2360	2520	2640
F-6[b]	58.1	27.8	1.4	[e]	12.7	0	2474	2517	2600
S[a]	41.2	13.1	15.8	0.6	14.9	14.4	1930	1990	2170
F-7[b]	48.0	15.3	19.3	[e]	17.4	0	1997	2025	2220
F-8[b,c]	42.9	13.7	17.3	[e]	15.6	13.0% H_2SO_4	1999	2041	2181
C-499[d]	38.4	14.3	23.2	1.7	7.9	14.5	2034	2080	2156
F-13[b]	44.5	16.6	29.7	[e]	9.2	0	2148	2196	2252
C-500[d]	59.4	25.9	1.2	1.2	8.1	4.2	2439	2569	Out of range
F-14[b]	61.7	26.9	3.0	[e]	8.4	0	2489	2554	Out of range
C-501[d]	50.8	28.2	2.7	1.8	13.8	2.7	2179	2376	2476
F-15[b]	52.6	29.2	3.9	[e]	14.3	0	2223	2437	Out of range
C-502[d]	31.1	16.3	2.8	1.7	47.7	0.4	1893	1989	2078
F-16[b]	31.4	16.5	3.9	[e]	48.2	0	1942	1982	2131

[a] Sample designation and data by Nicholls et al. of the Bureau of Mines (*13*).
[b] Illinois State Geological Survey Fuels Chemistry Laboratory serial numbers.
[c] Same as F-7 but contains H_2SO_4 corresponding to SO_3 content of ash sample S.
[d] Illinois State Geological Survey Analytical Laboratory coal sample serial numbers.
[e] MgO replaced by equivalent CaO which is included in the CaO column.

TABLE IV. FUSION TEMPERATURES OF ASH L AND OF OXIDE MIXTURE F-4 BY VARIOUS METHODS

Sample	Method and Reference	Softening Temp., ° F.	Difference, ° F. From L	Difference, ° F. From F-4
Ash L	Detd., Nicholls et al. (*13*)	2800	0	+280
Mixture F-4	Detd., Ill. State Geol. Survey	2520	−280	0
Ash L	Estd., Estep et al., Fig. 3 (*8*)	2675	−125	+155
Ash L	Estd., Estep et al., Fig. 15 (*8*)	2675	−125	+155
Ash L	Estd., Moody and Langan, Fig. 8 (*10*)	2650	−150	+130
Ash L	Estd., Nicholls et al., Fig. 7 (*13*)	2740	− 60	+220
Mixture F-4	Estd., Nicholls et al., Fig. 7 (*13*)	2840	+ 40	+320
Ash L	Estd., Demorest and Schaefer (*7*)	2700	−100	+180

minations of the fusion characteristics of the mixtures reported in Table III, it appears that the initial deformation temperatures and the fluid temperatures of the synthetic mixtures are high with respect to the softening temperatures when compared with the corresponding set of values for the natural ash. These relationships are more readily apparent from their graphical representation in Figure 4. It is suggested that these differences are due to the manner in which the components are present in the mixture; they are more closely associated with each other in the ash than in the oxide mixture. The initial deformation and the fluid temperatures are raised since they are, respectively, the temperature at which the first fluid material appears and that at which all of the material is fluid. Since the softening temperature is the temperature at which sufficient fluid material is present to make a viscous mass, it is less affected by the condition in which the component oxides exist. By the time the softening temperature is reached, opportunity has occurred for reactions to have taken place between the oxide components of the cone to form sufficient fluid. We assume then that the softening temperatures of mixtures of the four main oxides will correspond to the softening temperatures of corresponding natural coal ash. A study of that part of the four-component system in which Illinois coal ashes mainly lie is in progress.

Ash Composition and Initial Deformation Temperature

The initial deformation temperature of a coal ash is defined (*1*) as "the temperature at which the first rounding or bending of the apex of the cone takes place." Such deformation is presumably due to the formation of a slight amount of liquid material through the melting of the most easily fusible material in the ash. In a system in equilibrium, the first material to fuse, and conversely the last to freeze, is a eutectic. While conclusions from systems in equilibrium cannot be strictly applied to coal ashes which have not achieved equilibrium through fusion, fair proximations to equilibrium results would be expected in coal ash cones because of the intimate and uniform mixing of the finely ground ash. It would be expected that the initial deformation, softening, and fluid temperatures of eutectic compositions would be practically identical and that as the compositions of the mixtures increasingly deviate from eutectic composition these values would be farther apart. Because the four-component system lime, alumina, silica, and iron oxide is practically unknown, it is virtually impossible to obtain a direct proof of such a relationship. The writers believe that experimental work on synthetic mixtures in known parts of the system does substantiate the expectations. The results of the experimental work are presented in Table V.

Coal Mineral Matter and Clinkering

It is generally known that, although the ash-cone softening temperature is a fairly good indication of the comparative magnitudes of clinkering troubles under any given set of conditions, such indications are not always reliable. As is well known, clinkers result from the coalescence of fused and plastic ash particles into a solid but still usually heterogeneous mass. The clinker becomes stronger, denser, more vitreous, and more homogeneous in composition as the action proceeds. The quantitative and qualitative distribution of the mineral matter in the coal (and consequently of the ash) must have considerable influence upon the clinkering behavior of any coal. Radiographic examination shows that the mineral matter in not uniformly distributed, and petrographic examination shows that the relative proportions of the minerals may vary widely. These variations are reflected in the ap-

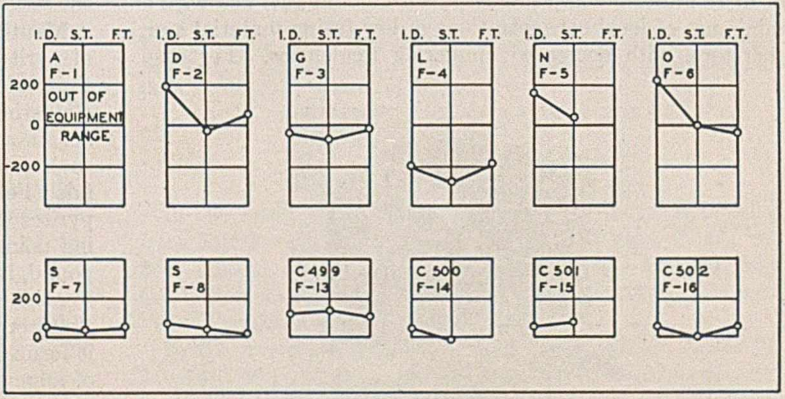

FIGURE 4. DEVIATIONS OF FUSION DATA FOR OXIDE MIXTURES FROM DATA FOR CORRESPONDING COAL ASHES

I. D. = initial deformation; S. T. = softening temperature; F. T. = fluid temperature.

TABLE V. INFLUENCE OF EUTECTIC OR MINIMUM MELTING COMPOSITIONS ON THERMAL BEHAVIOR OF CONES

Laboratory No.	Identity of Oxide Mixture	Composition SiO_2	Al_2O_3	CaO	Fe_2O_3	Lowest Fusing Material M. P.	Cone Initial deformation	Softening temp.	Fluid temp.
		%	%	%	%	° F.	° F.	° F.	° F.
C-1100	Eutectic[a]	42.0	20.0	38.0	..	2312	2230	2315	2341
C-1101	Compn. near eutectic[b]	33.0	27.0	40.0	..	2312	2293	2388	2424
C-1105	Min. melting solid soln.[c]	28.7	..	11.7	59.7	2048	2002	2039	2058
C-1106	75 parts C-1105 + 25 parts Al_2O_3	21.8	23.8	8.9	45.5	2048	2061	2201	2292
C-1107	Solid soln. in system Ca_2SiO_4–Fe_2SiO_4[d]	33.5	..	48.8	19.6	2246	2223	2313	2325
C-1108	75 parts C-1107 + 25 parts Al_2O_3	24.8	24.6	36.1	14.5	2246	2470	2517	2592
C-1113	Material of min. m. p.[e]	35.6	..	15.7	48.7	1999	1989	2008	2019
C-1115	90 parts C-1113 + 10 parts Al_2O_3	32.0	10.0	14.1	43.8	1999	1916	1941	1971
C-1116	75 parts C-1113 + 25 parts Al_2O_3	26.7	25.0	11.8	36.5	1999	2123	2214	2355

[a] Eutectic at the juncture of the fields of the primary phases anorthite, gehlenite, and pseudowollastonite in the system CaO–Al_2O_3–SiO_2 (*14*).
[b] Composition between the eutectic (note[a]) and gehlenite in the system CaO–Al_2O_3–SiO_2 (*14*).
[c] Composition having lowest melting point in the series of solid solutions from $CaFeSiO_4$ to fayalite in the system Ca_2SiO_4–Fe_2SiO_4 (*5*).
[d] Composition in the series of β-Ca_2SiO_4 solid solutions in which liquid appears at 2246° F., and which series ranges from 10 to 46 per cent Fe_2SiO_4. At 2280° F. the mixture is half liquid (*5*).
[e] Lowest melting composition in the system CaO–FeO–SiO_2 (*6*).

pearance of the ash skeleton left after the careful combustion of a block of coal (Figure 5). Such variable distribution must effect variations in softening temperatures. That it does is shown by the behavior of coal ash skeletons upon fusion (Figure 6). The temperature at which clinker formation starts depends upon the fusion temperature of that portion of the ash having the lowest softening temperature; its extent and rate depend on the quantity and viscosity of this easily fusible material and upon changes produced in the properties of the material previously melted by the incorporation of the more refractory material. Localizations of relatively easily fused material can, therefore, be a source of clinker trouble. It is known that in general an increase in iron oxide and lime lowers the ash-softening temperature. Iron oxide and lime are mainly derived from iron pyrites and from calcite, respectively, which both tend to be locally concentrated. These minerals are largely removed by cleaning processes, and their removal should in general, though not necessarily, increase the ash-softening temperature of the cleaned coal; this fact is borne out by the study of twenty-six coals by Nicholls, Selvig, and Ricketts (*13*).

Besides this general increase in ash-softening temperature due to lime and pyrite removal, we should expect a diminution in clinker troubles. That this is the case is also apparently verified by the results on two coals tested in the raw and washed state presented in the work just cited (*13*). In one case the ash-softening temperature of the average ash was lowered by washing, yet clinkering trouble decreased, as indicated by the percentage of the total ash in the form of clinker larger than 2 inches. This particular coal also furnishes evidence that clinkering is influenced by the heterogeneity of the ash. Crushed coal should produce an ash of more uniform composition throughout the fuel bed with a minimum of local concentrations of low fusing material and, therefore, with decreased clinkering tendencies. For easy reference, the values here referred to are reproduced in Table VI.

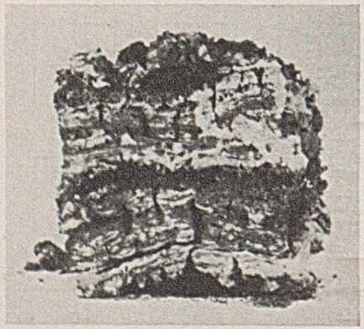

FIGURE 5. COAL ASH SKELETON

TABLE VI. INFLUENCE OF COAL WASHING AND CRUSHING UPON CLINKERING TENDENCIES OF RESULTING FUEL[a]

Coal	Treatment	Ash-Softening Temp., ° F.	Per Cent Total Ash in Form of: Clinker over 2 in.[b]	Clinker over 1/2 in.[b]
H	Raw	2600	32.0	65.6
H	Washed	2570	17.0	47.8
H	Raw, crushed	2600	9.3	48.0
H	Washed, crushed	2570	4.3	32.3
R	...	2470	29.7	53.3
R	Washed	2630	9.6	33.3

[a] Data from Nicholls, Selvig, and Ricketts (*13*).
[b] Av. of 20, 30, and 60 pounds per square foot per hour combustion rates.

Further confirmation of the influence of the variability of the coal ash upon clinkering may be found in the behavior of coke ash. Before being processed into coke, the coal, especially if blended, is crushed to a fairly small size of the order of 1/8 to 1/2 inch. Even though the resulting coke as burned may be 2 inches or larger in size, the largest ash group in which the ash structure is the same as in the original coal can be no larger than the size of the largest coal particle in the coke charge. In addition, the process of coking, involving swelling, flowage, and shrinkage, has further disrupted the original relationships of the ash components. The ash from cokes of high average ash-softening temperatures is notoriously more dusty and free from sintered material than is ash from the corresponding coal burned in lump form. When clinker does form from coke ash, especially from cokes of low average ash-softening temperatures, the clinker tends to form in vitreous sheets close to the grate bars because of the intimate mixture of all ash components.

Mention has previously been made in this paper of the role of pyrite in furnishing local concentrations of iron oxide in the coal ash. This is the sole influence of iron pyrites on clinkering. Iron sulfide itself (either FeS or FeS_2) does not act as a cementing material in clinker formation although such a cementing action is frequently attributed to iron sulfide (FeS) resulting from the thermal dissociation of iron pyrites (FeS_2). Iron sulfide (FeS) is reported to have a melting point of 2187° F. (1197° C.). Since it is a pure compound, it was expected to have a sharp melting point and not to exhibit a gluelike viscosity. It was found experimentally that iron sulfide did have such a sharp melting point and that it formed a very fluid liquid, giving the general impression of mercury. Iron sulfide was found to be incompatible with viscous fused compositions in the range of coal ash compositions. Oxide mixtures corresponding to a coal ash analysis (C-499) were made up and fused in a clay crucible and heated

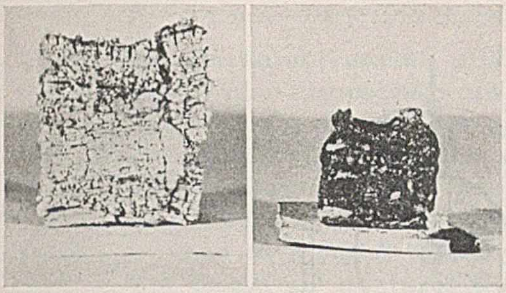

Figure 6. Skeleton of Coal Ash before and after Sintering

in an induction furnace. Iron sulfide was introduced either in the cold melt or into the viscous mass, and the viscous mass (2192° F., or 1200° C.) was stirred with a graphite or sillimanite rod. Portions of the melt removed on the end of the rod and cooled showed, on chemical test, that the iron sulfide was distributed in discrete particles throughout the mass. Upon pouring the melt from the crucible, the movement of the viscous silicate melt released to the surface globules of fluid iron sulfide which dropped out to an accompanying shower of sparks. That the globules were iron sulfide and not iron was proved by chemical test. The molten iron sulfide played no part in forming the viscous mass but was itself enclosed in it. The occurrence of iron sulfide in discrete particles was also found in the case of clinker or rather slag, resulting from the combustion of a low-grade, high-pyrite midwestern coal on underfeed stokers. This slag enclosed pieces of coke but was otherwise rather homogeneous in appearance except for exposed corners or protrusions which were vitreous. Analysis showed these vitreous portions to have the same composition as the remainder of the slag and, therefore, to have resulted from rapid cooling. This slag contained, roughly, 0.25 per cent sulfide sulfur and 40 per cent iron oxide. In general, the slag was very dark gray and microcrystalline. The application of hydrochloric acid to a freshly broken face resulted in the liberation of hydrogen sulfide from points or, rather, very small areas. Gas evolution from the points ceased after a short time. Further exposure of fresh surfaces exposed new sulfide particles. The total sulfide sulfur content of the slag is remarkably low compared to the iron oxide content, the origin of which is largely iron pyrite. The writers hold untenable the view that iron sulfide, derived from pyrite, is an important factor in clinker or honeycomb formation; but rather that the influence of iron pyrites in coal on clinkering is due to the localized increase in iron oxide resulting from its oxidation.

Conclusions

1. Coal ashes are contained in the four-component system lime–alumina–silica–iron oxide.
2. The separable mineral matter in the coals examined is composed mainly of the minerals pyrite, calcite, quartz, kaolinite, and detrital clay. Other minerals make up an insignificant portion of the separable mineral matter.
3. Softening temperatures of mixtures of the four oxides, lime, alumina, silica, iron oxide, in the proportion present in coal ash correspond to the softening temperatures of the respective natural coal ashes.
4. Initial deformation temperatures of oxide mixtures and therefore probably of coal ashes are related to the melting point of the eutectic or material of minimum melting point with which the given mixture is associated in the phase-equilibrium system.
5. The initial deformation, softening, and fluid temperatures of eutectic compositions are practically identical, and as the compositions increasingly deviate from eutectic compositions these values will increasingly deviate from the melting point of the eutectic.
6. The temperature at which clinker formation starts is dependent upon the fusion temperature of that portion of the ash having the lowest softening temperature. The extent and rate of the clinkering depends on quantity and viscosity of this easily fusible material, and upon the changes produced in the properties of the material previously melted by the incorporation of the more refractory material.
7. Localized concentrations of more readily fusible material increase the tendency toward clinker formation.
8. Iron pyrite or iron sulfide as such does not act as a cementing agent in clinker formation. The influence of pyrite or iron sulfide on the properties of coal ashes is due to the iron oxide resulting from their oxidation.

Acknowledgment

This work was carried on in the laboratories of the Illinois State Geological Survey. The authors wish to express their appreciation to Frank H. Reed, chief chemist, and to Gilbert H. Cady, senior geologist, Coal Division, for their coöperation and suggestions during the course of this work and the preparation of the manuscript. The authors also wish to express their indebtedness to O. W. Rees under whose direction the ash fusion determinations were made by J. W. Robinson.

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Correction

In the article by F. G. Straub entitled "Removal of Silica from Solution at Boiler Temperature" [Ind. Eng. Chem., 28, 36–7 (1936)], an error occurs on page 37 in the fifth line from the bottom in the first column. The figure "4.5" should read "45 millimoles per liter."

In the paper on "Analcite" by the same author [*Ibid.*, 28, 113–14 (1936)], the last sentence on page 114 should be changed to read: "These tests appear to indicate that, if the silica in solution in a boiler water is kept below 2.2 millimoles per liter (120 p. p. m.), analcite scale could be prevented."

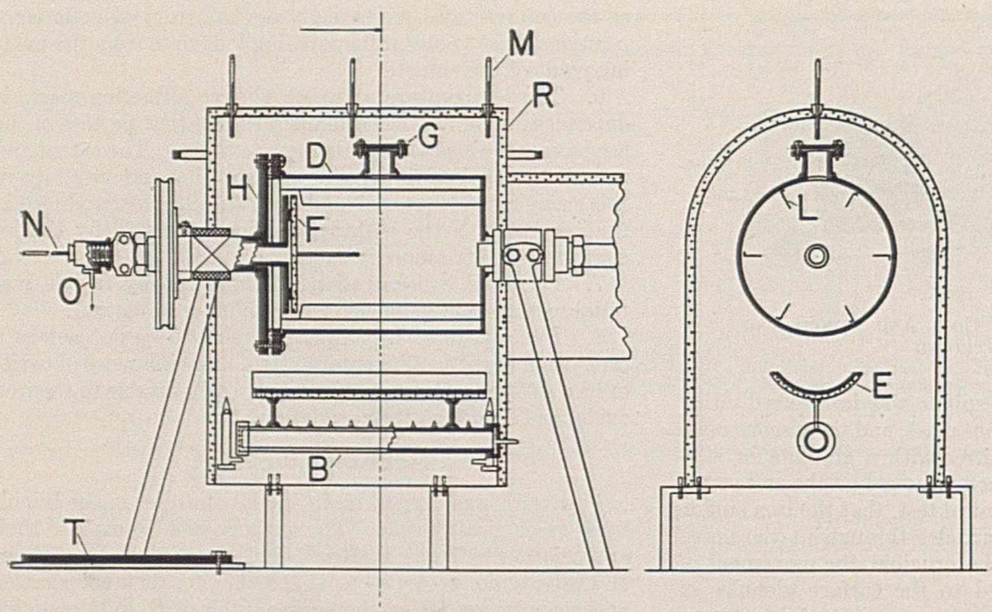

Figure 1. Steaming Drum Assembly

Seasoning of PORTLAND CEMENT at Elevated Temperature

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PREVIOUS work has shown that the effect of absorbed water vapor on the setting of Portland cement is pronounced and even more significant than the chemical effect of added calcium sulfate (*15*, *16*). The retarding action of water vapor apparently is associated with its activation of tricalcium silicate in cement. When the absorption is too great, a significant activation of tricalcium aluminate as well as of tricalcium silicate takes place, so that increasing amounts of water then are required for normal consistency, though the cement remains slow-setting (*16*).

In cement-finishing mills temperatures are high, and often more or less moisture may be present. Some moisture may be derived also from added gypsum. In evaluating natural anhydrite and gypsum as retarders of set, information on the effect of moisture on Portland cement at such temperatures as may occur in the mill was desirable. Hence in the present experiments the degree of absorption of water vapor at elevated temperatures was studied and the effect of such absorption on the setting and strength of the cement observed.

Previous Results

The tempering effect of moisture at elevated temperature has been recognized. Geyer (*12*) in a suggestive paper stated that quick-setting clinker could be made slow-setting with little loss in strength by the addition of water to the mill. In 1903 Bamber (*4*) patented the process of adding steam to the mill to obtain slow setting and in 1909 (*3*) discussed the beneficent effects, such as reduction of the gypsum requirement. Edison (*10*) patented the steam treatment of cement in a rotating vessel. Gadd (*11*) found that the slow setting obtained by the action of steam was more permanent than that due to added gypsum. Ware (*20*) wrote that only exposure to steam or water at elevated temperature could render certain cements slow-setting.

Opinion at present appears to be that, although the absorption of water vapor such as that due to exposure to steam may be useful in certain respects, it causes weakening of the cement. In the present work it was found that low strength did exist but only when the absorption of water vapor was excessive and beyond the point at which desired favorable effects were obtained.

Materials

Four clinkers, differing widely in composition were chosen. The analyses, together with the computed compound composition, oxide ratios, and fineness, are given in Table I. The alkalies were determined directly by a method described else-

Powdered Portland cement absorbed water vapor from an atmosphere of steam at temperatures above the dew point. The absorption was rapid in the course of the first few minutes and increased slowly thereafter. The amount of absorption was determined at a series of temperatures. For steam-air mixtures the absorption depended within limits only on the ratio of absolute temperature of exposure to that of the dew point.

Comparison was made of the setting and strength of clinkers which had absorbed different amounts of water vapor (different seasoning). Progressive seasoning up to the thoroughly seasoned state changed the setting from quick to slow and decreased continuously the water required for normal consistency. The 1:3 mortar tensile strength was very nearly constant. Corrected for the effect of added gypsum, the strength of three out of four clinkers was least in the case of the least seasoned specimen. Resistance to the action of carbon dioxide at room temperature was greatest for thoroughly seasoned clinkers. The effect of additions to such clinkers was observed.

The degree of seasoning was for all clinkers related similarly to the temperature of exposure to the superheated steam. At temperatures too close to the dew point the absorption of water vapor was excessive, resulting in the production of an overseasoned state. Overseasoned cements required an excess of water for consistency and yielded mortar of relatively low strength.

The probable advantages of a controlled seasoning process are discussed.

where (*5*). The clinkers were crushed and ground in the laboratory until their surface area as measured by an air analyzer (*18*) was greater than that for ordinary cement. Except for clinker *Pd*, which had a high initial loss, the ignition loss of all clinkers increased appreciably after pulverizing, as seen from Table I.

The gypsum and $CaCl_2 \cdot 2H_2O$ were c. p. products whose purity was checked petrographically. The gypsum was slightly finer than the clinkers. The calcium chloride was ground to pass a 200-mesh sieve. The plaster was prepared by heating the gypsum for several hours at 130° C.

Apparatus

The apparatus in which the cements were exposed to steam or steam-air mixtures is shown in Figure 1:

It consisted of a metal drum, *D*, about 9 inches (22.8 cm.) wide and 12 inches (30.5 cm.) long, rotating at 50 r. p. m. The interior was provided with lifts *L* to raise the cement and shower it through the stream of vapor. Head *H* was bolted to the flanged end of the drum, with a narrow asbestos-composition gasket to prevent leakage. The cement was removed from the open end of the drum after sliding back *H*. Cement could be placed in the drum through its open end or through gasketed opening *G*. Head *H* and its bearing together with motor and pulley drive were mounted on a flat plate that could be slid back and forth along a track, *T*. The track and front bearing supports were screwed to a wooden frame that in turn was bolted to the floor.

The inlet and outlet of the drum were provided with stuffing nuts. Attached to the outlet pipe and within the drum was a circular disk filter, *F*, of diameter nearly equal to that of the inside of the drum. The filter material was cloth. Attempts to secure filtration by using a glass-wool plug in the hollow shaft failed because of inadequate filtering surface; considerable pressure built up when the cement was present in larger quantity. The steam or steam-air mixture left through outlet *O*.

Heat was provided by horizontal burner *B*, with two auxiliary burners at either end of the drum to provide heat for the end faces. The flame from burner *B* was kept out of direct contact with the drum, and the hot flue gas was distributed by baffle *E*, which consisted of a concave sheet-metal plate with an asbestos pad at the bottom. Surrounding the drum was a removable asbestos cover, *R*, which retained the mixture of hot flue gas and excess air rising up from below and protected the drum from contact with cold air. Three thermometers, *M*, were placed in the cover near the top and the burners adjusted so that they all read approximately the same temperature.

The temperature within the drum was measured by a calibrated thermometer, *N*, of extra length such as is provided for drying ovens. The stem of the thermometer passed through the hollow shaft snugly through a hole in the filter.

Steam was generated in a flask placed over an electric hot plate. It passed through a heavy cast-iron gas-fired superheater (not shown in Figure 1). An air line into the superheater provided for air-steam mixtures. The superheater and the heated pipe lines leading to the drum were shielded with asbestos covers and thermometers placed in or around the line along its length. Air flow was measured by means of a flowmeter calibrated against a calibrated wet-test meter. The steam flow was determined from the rate of flow of condensed water at a point between the flask and superheater.

Procedure

In making a run, the temperature of the superheater and of the drum was raised rapidly to within several degrees of the desired temperature, then the burners were lowered approximately to their final setting. The superheater temperature was maintained at or slightly above that in the drum. About 5 liters of air per minute were passed through the apparatus; when in the course of an hour the temperature in the drum had remained stationary for some time at a value slightly above that desired, steam was added to the air at about 5 liters per minute. After 5 or more

TABLE I. ANALYSIS OF CLINKERS (IN PER CENT)

	Ua	*Pd*	*Ha*	*Ls*
Ignition loss[a]	0.08	1.43	0.13	0.24
Ignition loss[b]	0.35	1.43	0.60	0.88
Insoluble	0.04	0.19	0.09	0.12
SiO_2	21.54	22.52	23.89	20.96
Al_2O_3	6.98	5.39	5.12	7.05
Fe_2O_3	3.10	2.73	3.66	4.13
CaO	63.34	65.41	65.09	64.85
MgO	3.23	1.99	1.44	0.95
SO_3	0.35	0.62	0.01	0.29
K_2O	0.48	0.22	0.42	0.23
Na_2O	0.61	0.63	0.25	0.76
$3CaO \cdot SiO_2$	41	53	43	50
$2CaO \cdot SiO_2$	30	24	36	23
$3CaO \cdot Al_2O_3$	13	10	7	12
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	9	8	11	12
$CaO/SiO_2 + R_2O_3$	2.00	2.14	1.99	2.02
SiO_2/R_2O_3	2.14	2.78	2.72	1.87
SiO_2/Al_2O_3	3.09	4.18	4.67	2.97
Surface area, sq. cm./gram	2200	2720	2500	2360 (Ls_1) 3360 (Ls_2)

[a] On crushed clinker.
[b] On powdered clinker as used for test.

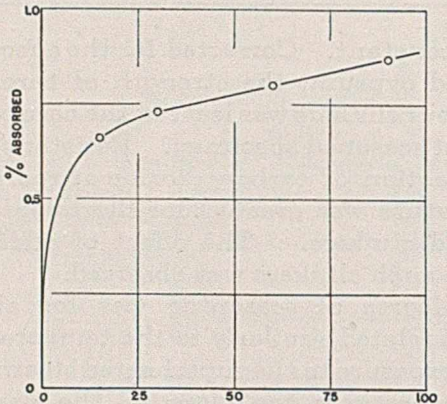

Figure 2. Relation between Time of Exposure and Absorption of Water Vapor by *Ua* Clinker

minutes the air was shut off and steam alone was passed through for 10 minutes to clear out the air. Thereafter, time-temperature readings were taken.

Temperature control was manual. The gas flow was adjusted with reference to a draft gage or by noting the height of the flame. By holding the temperature of the thermometers in the insulating hood constant to within 2° or 3° C., it was possible to regulate the temperature of the thermometer in the rotating drum easily to within 0.5° C.

At the end of the run all burners were raised, and air was introduced at 5 liters per minute. When the temperature in the drum had risen about 3°, the steam was shut off, the air flow was increased to about 15 liters per minute, and the burners were lowered so that the temperature in the drum did not exceed the treating temperature by more than 15°. The flow of air was continued until all vapor was out of the drum.

When a run was made with a steam-air mixture, a similar procedure was followed. The steam flow in this case was calibrated before and after each such run to allow for possible fluctuations due to changing room temperature.

Method of Test

The freshly ground clinkers were kept in lard cans sealed with tape. The procedure in mixing the various additions of gypsum was the same as that described previously (*15*). Test specimens were stored in a forced-draft moist cabinet automatically controlled at 70° F. (21.1° C.) The temperature of the room was maintained within a few degrees of 70° F.

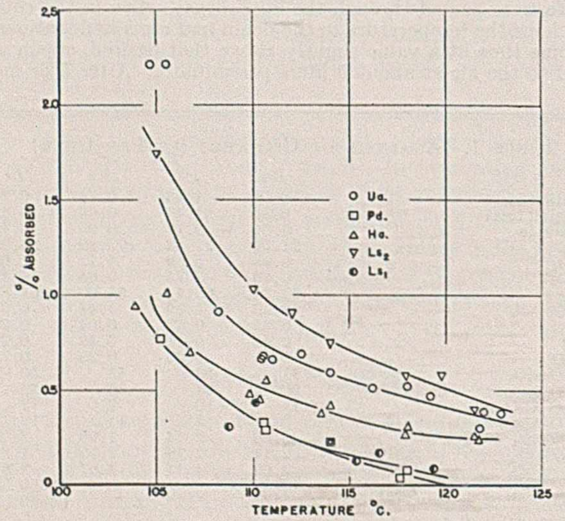

Figure 3. Relation between Temperature of Exposure and Absorption of Water Vapor

Owing to the limited amount of cement available, a consistency and setting-time test using small samples was developed:

> To a cratered 10-gram sample of cement was added water from a 5-cc. Mohr pipet. The cement and water were mixed rapidly with a small spatula, and the mixture was kneaded with the fingers, protected with tight-fitting rubber cots. The total time from the addition of the water was 1 minute. After consolidation of the paste by rolling between the palms it was placed in a metal cylinder 23.5 mm. i. d. and 12.5 mm. high, and the surface of the pat was gently leveled. The ordinary Vicat apparatus was used for test, except that for the consistency test the needle was replaced by a metal rod 4.8 mm. wide and 50 mm. high. Normal consistency was found by trial to correspond to 6-mm. penetration of the rod after 15 seconds. Initial set corresponding to that with the large batch was secured when the needle penetrated 2 mm. In making both the consistency and set tests, the rod or needle after leveling to the surface of the pat was released by quickly turning the set screw. The percentage for consistency could generally be specified to 0.5 per cent and the initial setting time to 15 minutes. It was not feasible to measure final sets in this method of test, but for all clinkers it was evident that final set would occur within 6 or 7 hours.

Rate of Absorption of Water Vapor

The absorption of water vapor after exposure to the superheated steam was measured by the loss on ignition at 1000° C. for 30 minutes, always using an untreated sample for comparison.

Preliminary tests showed that the rate of absorption on exposure to steam decreased rapidly with time. Results of a careful run on 500 grams of *Ua* clinker are shown in Table II and Figure 2. A rapid absorption took place during the first few minutes; absorption increased slowly thereafter with time. At the end of 10 minutes the absorption was more than 75 per cent that at the end of 90 minutes.

Table II. Relation between Time and Absorption of Water Vapor for *Ua* Clinker

Temp. ° C.	Time Min.	Total Time Min.	Absorption Per cent
111.0	15	15	0.66
111.3	15	30	0.73
110.7	30	60	0.80
110.9	30	90	0.87

Absorption of Water Vapor vs. Temperature

The clinker was exposed to steam for 15 minutes at a given temperature, a sample withdrawn, and the residue reëxposed for the same time at a next lower temperature. In view of the initial rapid rate of absorption it is believed that the results obtained in this way approximate the long-time absorption at any given temperature. The charge of powdered clinker ranged from 500 to 2000 grams. Within the limits of error no difference in the absorption could be detected when the amount of material was varied within these amounts.

The results for several clinkers given (Table III and Figure 3) show that the amount of water vapor absorption at any temperature increased with decrease in temperature. The absorption increased at a more rapid rate than the temperature decreased, especially below about 110° C. As temperatures a few degrees above the dew point were approached, the absorption became great and increased rapidly as the temperature was further lowered.

From the data obtained in different runs the temperature for any given absorption could be specified to within less than 2° C. Variations were due in part to the somewhat uncertain correction for prior exposure of the stored clinker to the atmosphere, as discussed later.

TABLE III. RELATION BETWEEN TEMPERATURE AND WATER VAPOR ABSORPTION

Ua Temp. ° C.	*Ua* Absorption %	*Ha* Temp. ° C.	*Ha* Absorption %	*Pd* Temp. ° C.	*Pd* Absorption %	*Ls₁* Temp. ° C.	*Ls₁* Absorption %
116.2	0.51	121.7	0.24	121.5	−0.04	119.4	0.09
112.5	0.69	117.9	0.27	118.0	+0.08	115.3	0.13
108.2	0.91	114.0	0.42	114.0	0.23	110.1	0.44
105.5	2.21	110.6	0.55	110.6	0.29		
		105.6	1.01	105.2	0.77	116.5	0.17
						108.7	0.30
122.1	0.39	121.5	0.26	121.0	−0.04		
111.0	0.66	118.0	0.31	117.6	+0.04		
104.7	2.12	113.5	0.38	114.0	0.23	*Ls₂*	
		110.3	0.45	110.5	0.33	121.5	0.40
129.0	0.10	103.9	0.94			117.9	0.58
122.9	0.38			104.5	(1.61)	114.0	0.75
119.2	0.47	109.8	0.48			110.0	1.03
110.4	0.66	106.7	0.70			105.0	1.74
121.7	0.30						
118.0	0.52					119.8	0.58
114.0	0.59					112.0	0.91
110.5	0.68						

As a check on the temperature-absorption data obtained with the rotating drum, analogous runs were made with about 1 gram of sample contained in a glazed porcelain boat which had previously been tested for water absorption. The boat was placed in the center of a horizontal glass tube set in an electrically heated furnace which was controlled by a one-point recorder and in advance of which was a ribbon-wound superheater. Temperatures of the furnace were measured at the steam inlet and outlet, and adjustment was made until approximate equality of temperature was obtained. The amount of water vapor absorbed was determined by weighing the boat before and after the run. Table IV shows the results for *Ua* clinker. By comparison with Table III it is seen that except for the point at 113.5° C. the agreement in the temperature-absorption data is as good as could be expected under the dissimilar conditions of test.

Figure 3 shows that the water absorption curves for different clinkers run roughly parallel. The displacement is due to the difference in clinker composition and, more noticeably, to the effect of varying fineness and different previous absorption during storage.

TABLE IV. ABSORPTION OF WATER VAPOR BY *Ua* CLINKER CONTAINED IN A PORCELAIN BOAT

Temp., ° C.	Absorption, %	Temp., ° C.	Absorption, %
119.2	0.35	110.4	0.75
113.5	0.44	106.5	1.10
109.7	0.67	104.5	1.58

Increasing the fineness increased the water absorption. At 110° C. the absorption by *Ls*₁ was 0.40 per cent; *Ls*₂, the same clinker ground finer, absorbed 1.03 per cent. The surface area of *Ls*₂ was 3360 square cm. per gram, and of *Ls*₁, 2360 square cm. per gram (Table I). These figures show that the absorption increased over one and one-half times faster than the surface area. This may be due to a selective concentration of more absorbent mineral constituents such as $3CaO \cdot SiO_2$ in the finer sizes with increased grinding (cf. *9*) or, in so far as complete equilibrium was not attained, to a greater specific rate of reaction of the finer sizes (cf. *17*).

Absorption of water vapor from the atmosphere during storage also influenced the amount of absorption on exposure to steam. The powdered clinker had been stored in lard cans sealed with tape; nevertheless, their loss on ignition increased continuously, due in part to exposure incident to the removal of samples. The absorption of water vapor at elevated temperature by the stored clinker was less than that of the fresher clinker. Hence, in order that determinations made at different times might be compared, the absorption at elevated temperature was corrected for storage of the clinker by referring back to the loss on ignition of the clinker as first used. The data of Table III have been corrected in this manner; the maximum correction amounted to about 0.1 per cent.

The low absorptions for clinker *Pd* are due to the high loss on ignition, 1.43 per cent, of the uncrushed clinker. Clinker *Pd* actually suffered a loss at temperatures above 120° C.; below this temperature it absorbed moisture as usual but to a lesser extent than any of the other clinkers.

By comparing the loss on ignition after exposure instead of percentage absorption, small differences in the initial ignition loss were compensated, and the curves drew together. This is shown in Figure 4, in which the loss on ignition after exposure to steam at a given temperature was the same to within 0.2 per cent for different clinkers with similar fineness. In two cases it was appreciably higher—clinker *Pd* with a high initial loss on ignition and clinker *Ls*₂ ground unusually fine.

Absorption from Steam-Air Mixtures

The absorption of water vapor from a 1:3 and 1:1 steam-air mixture is compared with absorption from pure steam (1:0) in Table V and Figure 5. The time of exposure with the mixture was the same as with 100 per cent steam.

TABLE V. ABSORPTION OF WATER VAPOR FROM STEAM-AIR MIXTURES FOR CLINKER *Ua*

100% Steam (Dew Point, 100° C.)			50% Steam (Dew Point, 81.7° C.)			25% Steam (Dew Point, 65.4° C.)		
Temp. ° C.	T/T_s	Absorption %	Temp. ° C.	T/T_s	Absorption %	Temp. ° C.	T/T_s	Absorption %
121.7	1.058	0.30	102.0	1.058	0.32	85.0	1.058	0.17
118.0	1.048	0.52	98.7	1.048	0.48	81.9	1.048	0.28
114.0	1.038	0.59	95.0	1.038	0.61			
110.5	1.028	0.68	91.5	1.028	0.84	76.3	1.034	0.57
108.2	1.022	0.91				73.0	1.022	0.86
104.7	1.012	2.12	86.1	1.014	1.03	70.4	1.015	1.10

All points fell approximately on the same curve in a plot of the absorption against T/T_s, where T is the absolute temperature of absorption and T_s the absolute temperature of the dew point. It would be expected that, in so far as complete equilibrium was not reached, the absorption would fall off at the lower partial pressures. There is some indication of this for the 25 per cent steam mixture.

Expression of the absorption as a function of T/T_s is derived by analogy with the expression obtained by Trouton

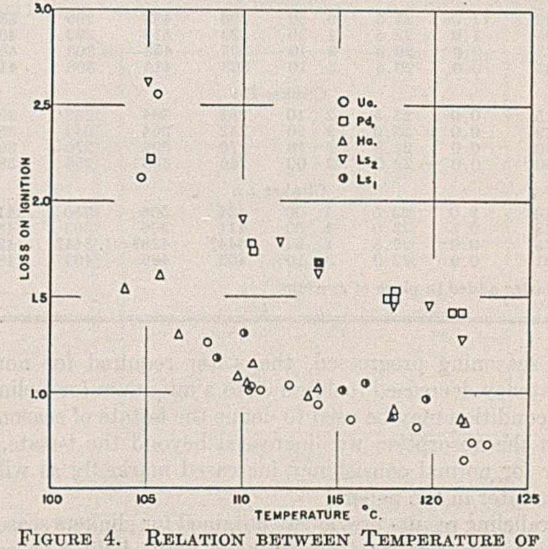

FIGURE 4. RELATION BETWEEN TEMPERATURE OF EXPOSURE AND SUBSEQUENT LOSS ON IGNITION

and Poole (*19*) for the absorption of water vapor by cotton. They found that at a given temperature,

$$w = f\,(P/P_s)$$

where w = weight absorbed
P = pressure
P_s = saturation pressure

Since $P/P_s = T/T_s$, $w = f(T/T_s)$—i. e., the amount absorbed at equilibrium is a function only of the ratio of the absolute temperature of absorption to that of the dew point.

The setting of clinkers exposed to steam-air mixtures was similar to that when exposed to pure steam. Selective activation of tricalcium silicate or tricalcium aluminate could not be observed definitely.

Setting and Strength vs. Progressive Absorption to t-State of Seasoning

It was previously observed (*16*) that Portland cement on exposure to moisture at room temperature is seasoned progressively whereby the setting is slowed until an optimum state of slow setting is reached. This was called the thoroughly seasoned, or, for brevity, the t-state of seasoning. Absorption of water vapor beyond this state resulted in an undesirable overseasoning (o-state of seasoning). Similar but more pronounced phenomena were observed in the present work at elevated temperatures.

Table VI shows the average data on setting and strength of four clinkers seasoned by exposure to superheated steam as already described. As the absorption of water vapor increased (Column 1), seasoning progressed until the t-state was reached approximately at the maximum absorption shown in Table VI for each of the clinkers. The absorption required to reach the t-state ranged from 0.3 to 0.9 per cent; this would be as much as 0.7 per cent more if the initial state had not corresponded to a clinker that had suffered exposure to the atmosphere during storage.

Table VI. Strength of Cement Progressively Seasoned up to the t-State

Absorption	Added Gypsum	Water for Normal Consistency	Initial Set		Tensile Strength 3-day	Tensile Strength 7-day	Corrected Tensile Strength 3-day	Corrected Tensile Strength 7-day
%	%	%	Hr.	Min.	Lb./sq. in.			
				Clinker *Ua*				
0.35	2.0	23.0	1	40	291	392	217	298
0.52	1.0	22.5	2	00	291	403	254	356
0.61	0.0	22.0	1	30	259	397	259	397
0.68	0.0	21.5	1	40	273	357	273	357
				Clinker *Pd*				
0.00	1.0[a]	23.0	0	50	306	433	269	386
0.08	1.0	22.5	1	30	329	515	292	468
0.23	0.0	20.5	2	10	303	463	303	463
0.33	0.0	20.5	2	10	308	416	308	416
				Clinker *Ha*				
0.25	0.0	23.5	2	10	282	394	282	394
0.29	0.0	23.0	2	20	242	364	242	364
0.40	0.0	22.5	2	10	270	396	270	396
0.50	0.0	22.0	2	00	256	385	256	385
				Clinker Ls_2				
0.40	2.0	23.5	1	00	424	506	350	412
0.58	0.5	23.0	1	00	411	506	393	483
0.75	0.0	22.5	1	50	344?	428?	344?	428?
0.91	0.0	22.0	2	10	403	489	403	489

[a] Plaster added in place of gypsum.

As seasoning progressed, the water required for normal consistency decreased (column 3) to a minimum for t-clinker. This condition may be used to define the t-state of seasoning. When the absorption was increased beyond the t-state, the water for normal consistency increased markedly as will be shown later in the paper.

Paralleling results previously obtained for clinkers seasoned at room temperature (*15*), fresh or very slightly seasoned clinkers were quick-setting and no addition of gypsum or plaster could make them slow-setting. After a certain degree of absorption of water vapor at elevated temperature, the clinkers became slightly seasoned, and, while quick-setting of themselves, could be slowed by gypsum. The second column of Table VI gives the addition of gypsum, or plaster if gypsum was not effective, required to bring about slow setting. With increased absorption of water vapor and consequent further seasoning, all clinkers had become slow-setting of themselves and no addition was any longer required (column 2). Clinker *Ha*, though practically quick-setting when fresh, required no addition at any degree of seasoning. As seen from Table I this clinker had a high SiO_2 to R_2O_3, SiO_2 to Al_2O_3, and $3CaO{\cdot}SiO_2$ to $3CaO{\cdot}Al_2O_3$ ratio, and also an unusually low $K_2O + Na_2O$ content. These are conditions (*16*) under which a minimum of retarder, if any, would be required.

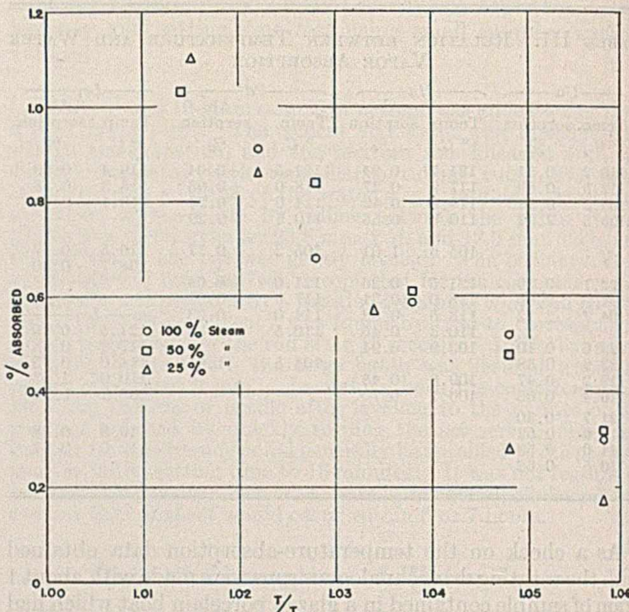

Figure 5. Absorption of Water Vapor from Steam-Air Mixtures by *Ua* Clinker

In comparing quantitatively the time of set, it should be borne in mind that the less seasoned states required more mixing water and in general also an addition of gypsum. Under these conditions, for clinkers *Ua* and *Ha* a faint maximum in time of set appeared at an intermediate state of seasoning. This result is inconclusive, however, because the differences are nearly equal to the average error. For clinkers *Pd* and Ls_2 the most seasoned states were decidedly the most slow-setting.

The temperatures of exposure required to bring about the above changes were similar for all the clinkers tested. With an exposure time of about 20 minutes, slow set could just be brought about by gypsum addition at 121° ± 2° C.; no gypsum was required for slow set at 115 ± 2° C.; the clinker was seasoned to the t-state at 111° ± 2° C.; below this temperature the clinker was undesirably overseasoned.

The fifth and sixth columns of Table VI give the 3- and 7-day 1:3 mortar tensile strength (pounds per square inch). Noting that gypsum has been added to the less seasoned states to render them slow-setting, a slight fall in strength is indicated as the t-state is approached.

However when correction is made for the effect of the gypsum, the picture is somewhat changed. In Table X is compared the strength of slow-setting t-clinker with and without 1.5 per cent addition of gypsum. The gypsum made a definite contribution to the tensile strength of all clinkers.

This averaged for the three clinkers studied 37 pounds at 3 days and 47 pounds at 7 days per 1 per cent gypsum added; the average deviation in the above figures was about 10 pounds. In order to make comparison on the basis of equal gypsum content, the above factors for gypsum may either be added to the slow-setting states or subtracted from the quick-setting ones. If in the latter case subtraction is made from the strengths shown in columns 5 and 6 of Table VI, the results shown in columns 7 and 8 are obtained. With the exception of slow-setting clinker *Ha*, the strength corrected for the effect of gypsum, or the intrinsic strength, was for the least seasoned state appreciably lower than for the succeeding more seasoned states. It would appear therefore that maximum intrinsic strength is attained only after a certain minimum degree of seasoning.

Effect of Carbon Dioxide on Differently Seasoned States

The action of carbon dioxide at room temperature was observed by placing 10-gram samples in each of a series of 100-cc. Erlenmeyer flasks and exposing to a stream of carbon dioxide bubbled through 65 per cent sulfuric acid. After 20 minutes of flushing, the flasks were shaken at 5-minute intervals for 1 hour.

Results for differently seasoned specimens of four clinkers are shown in Table VII. As in Table VI, gypsum or plaster was added to the partially seasoned clinkers to render them slow-setting. In certain cases the figures in parentheses are the actual amounts of water used, the water for normal consistency being estimated. In these instances the cement appeared plastic but stiffened rapidly. To reach normal consistency by a further addition of water was impractical or impossible.

TABLE VII. RESISTANCE TO EXPOSURE TO CARBON DIOXIDE AT ROOM TEMPERATURE AS FUNCTION OF SEASONING PROGRESSIVELY UP TO THE t-STATE

Absorption of Water Vapor	Addition	Before CO_2: Water for normal consistency	Before CO_2: Initial set	After CO_2: Water for normal consistency	After CO_2: Initial set
%	%	%	Hr. Min.	%	Hr. Min.
		Clinker *Ua*			
0.40	1.0 plaster	21.0	1 40	25.0 (23.0)	0 20
0.51	1.0 gypsum	21.5	1 50	23.5	1 40
0.64	0.0	21.0	1 20	22.0	1 10
0.68	0.0	21.0	1 40	21.5	1 10
		Clinker *Pd*			
0.00	1.0 plaster	23.0	0 50	24.0	1 00
0.03	1.0 gypsum	22.5	1 50	23.5	2 10
0.22	0.0	20.5	2 20	21.5	2 20
0.32	0.0	20.5	2 30	21.0	2 20
		Clinker *Ha*			
0.00	0.0	23.0	0 40	28.0 (25.0)	0 00
0.26	0.0	23.0	2 00	25.0	2 10
0.31	0.0	22.0	1 50	24.0	1 50
0.38	0.0	21.5	1 30	21.5	2 20
0.45	0.0	22.0	1 50	22.5	2 40
		Clinker *Ls*$_2$			
0.40	2.0 gypsum	23.5	0 40	28.5 (26.0)	0 30
0.58	0.5 gypsum	23.0	1 00	28.0 (26.0)	0 50
0.75	0.0	22.5	1 50	26.0	1 40
0.91	0.0	22.0	2 10	25.0	2 30

The exposure to carbon dioxide increased the water for normal consistency. This increase was greatest for the least seasoned state and least for the most seasoned state. The setting time in general was decreased slightly; with the least seasoned specimens the decrease resulted in definite quick-setting in certain cases. It appears therefore that the more seasoned states are most resistant to the action of carbon dioxide at room temperature, and hence to the atmosphere. This conclusion is in agreement with previous observations (*11*, *16*).

Overseasoning

When the clinker was exposed at temperatures too close to the dew point, an excess of water vapor was absorbed and the clinker became overseasoned. After such exposure the clinker was generally caked into small soft aggregates to an extent depending on the degree of absorption. The clinker was therefore put through a 28-mesh sieve and mixed before testing. The overseasoned clinker was characterized by an increase in the water required for normal consistency over the minimum required for t-clinker. Nevertheless, the o-clinkers were slow-setting, about equal to that for the t-clinker or slower. The slow set with increased water requirement corresponds to significant activation of tricalcium aluminate as well as of tricalcium silicate in the cement (cf. *16*).

TABLE VIII. RELATION BETWEEN WATER FOR NORMAL CONSISTENCY AND ABSORPTION OF WATER VAPOR BY OVERSEASONED CLINKER

Ua: Water for N. C.[a]	*Ua*: Absorption	*Pd*: Water for N. C.	*Pd*: Absorption	*Ha*: Water for N. C.	*Ha*: Absorption	*Ls*$_1$: Water for N. C.	*Ls*$_1$: Absorption
%	%	%	%	%	%	%	%
21.5	0.76	20.5	0.30	22.0	0.45	21.0	0.33
23.0	1.35	22.0	0.50	23.0	0.76	22.0	0.59
30.0	2.07	23.0	0.77	26.0	1.01	24.0	1.01
34.0	3.12	28.0	1.50	31.0	2.42	25.0	1.40
		34.0	2.48			29.5	2.01
		39.5	3.50			33.0	2.27

[a] N. C. = normal consistency.

Table VIII and Figure 6 show the relationship between the water for normal consistency and the absorption of water vapor for overseasoned clinkers. In these experiments the paste was kneaded vigorously for 2 minutes after the mixing water was added. The water for normal consistency was estimated in these earlier experiments rather than measured with the rod. If the kneading had been shorter or less vigorous, the water for normal consistency would have been uniformly higher or perhaps even a false set would have been induced.

The water for normal consistency increased continuously up to one and one-half to two times the minimum requirement with increase in absorption of water vapor by the overseasoned clinker. The curves of Figure 6 indicate that the water for consistency increases to an upper limit with increase in absorption.

The tensile strengths of o-seasoned and t-seasoned clinkers are compared in Table IX. As predicted previously from the voluminous nature of the pat of o-seasoned cement (*16*), the strength of o-clinker was decidedly less than that of t-clinker. This is true for all ages up to 28 days. A similar low strength

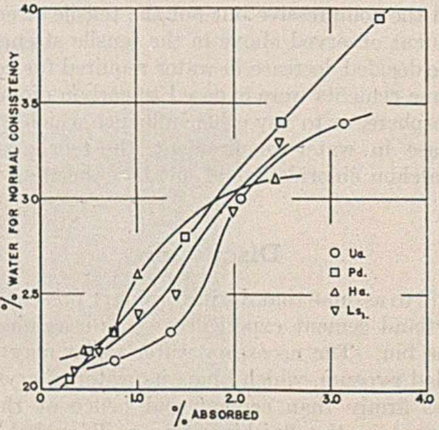

FIGURE 6. RELATION BETWEEN ABSORPTION OF WATER VAPOR BY OVERSEASONED CLINKER AND WATER FOR NORMAL CONSISTENCY

for cements containing excess absorbed water vapor recently was reported by Blank (*6*).

TABLE IX. TENSILE STRENGTH OF t-SEASONED AND o-SEASONED CLINKER

Clinker	State of Seasoning	Absorption	Water for Normal Consistency	Tensile Strength 3-day	Tensile Strength 7-day	Tensile Strength 28-day
		%	%	*Lb./sq. in.*	*Lb./sq. in.*	*Lb./sq. in.*
Ua	t	0.95	22.0	274	344	416
	o	1.81	28.0	173	221	330
Pd	t	0.30	22.0	288	380	482
	o	0.89	25.0	235	335	452
Ha	t	0.31	22.0	268	380	451
	o	1.06	25.5	230	306	406
Ls_1	t	0.10	22.0	338	465	510
	o	1.67	29.0	235	330	423

Effect of Additions on Strength of t-Clinker

Table X shows the effect on slow-setting t-clinkers of adding 1.5 per cent each of gypsum, plaster, and $CaCl_2 \cdot 2H_2O$. The addition of calcium chloride caused a decrease of 2.0 to 4.0 per cent in the percentage of water required for normal consistency and still more when working to equal mortar consistency (figures shown in parentheses). Both the 1.5 per cent plaster and the 1.5 per cent calcium chloride decreased the time of setting, the decrease being greatest with the plaster. The 3-day tensile strength was increased most by adding calcium chloride; the 7-day strength was, on the average, increased about equally for all the additions.

Exposure of the t-clinkers to carbon dioxide at room temperature destroyed the favorable effect of calcium chloride on the water for normal consistency. This is shown in Table XI. In the fourth column of Table XI the water used for normal consistency was estimated from the water actually used (given in parentheses). After exposure to carbon dioxide the water for normal consistency increased 2 to 9 per cent for all clinkers. The increase was greatest for clinker Ls_2 just as for t-clinker without calcium chloride addition after exposure to carbon dioxide (Table VII). With clinkers *Ua* and Ls_2 the carbon dioxide caused not only a marked increase in the water requirement but also a reversion to quick setting. These clinkers (Table I), from their higher alkali content and their less favorable composition ratios would be expected to be more prone to quick setting than clinkers *Ha* or *Pd*. Furthermore, clinker Ls_2 was ground unusually fine and would be more susceptible to unfavorable influences for this reason alone.

Platzman (*13*) reported that adding calcium chloride improved the compressive but not the tensile strength. The improvement observed above in the tensile strength may be due to the decided decrease in water required for consistency. If the same cements were exposed to carbon dioxide, or to a dry atmosphere, or to any other influence which would cause an increase in water requirement, the tensile strength on adding calcium chloride would not have been so much augmented.

Discussion

It is safe to assume that during ordinary present-day operation, Portland cement experiences some seasoning before it enters the bin. The necessary water vapor may be derived from added gypsum, which binds its water of crystallization much less firmly than cement and hence at the elevated temperatures in the finishing tube mill probably releases part of its bound water to the clinker as well as to the air. Vaporization of the moisture that often accompanies the clinker after it leaves the storage pile also may supply water vapor. If temperature conditions are favorable, a portion of this entrained moisture will be absorbed by the cement.

Controlled seasoning naturally has an advantage over chance seasoning that may be attained in ordinary practice. With controlled seasoning a uniform product is obtained, whereas this is not true for chance seasoning. It is usually necessary in practice to add nearly the maximum allowable quota of gypsum in order to obtain slow setting. Hence, the seasoning inadvertently acquired in the mill is highly limited and possibly is less than that minimum degree of seasoning apparently required for optimum strength. However, detrimental overseasoning might occur (*6*).

In the case of finely ground cement the degree of seasoning imparted by gypsum and adventitious moisture often will not prevent quick setting. Thus, with the usual gypsum addition, quick-setting difficulties appear as soon as the cement is ground too fine. This condition may be overcome entirely by controlled seasoning. The way is thus cleared for the practicable production of finely ground cement of high strength.

Ls_2, finer ground than Ls_1, showed a higher mortar tensile strength than the coarser clinker (Table VI and IX). Likewise, all the present clinkers showed higher intrinsic strength (corrected for gypsum addition) than the coarser commercial cements tested (Tables VI and XII). However, the differences in strength were probably not as great as might be realized if the fineness of the admixed sand had been adjusted to the cement. Effective utilization of a fine cement implies proper adaptation of the sand to cement. The more finely ground the cement the finer the sand should be if the ratio of cement to sand is kept the same; otherwise a condition exists in which the coarse pores of the sand are filled merely with many instead of with few hardened cement particles, and the main advantage of the larger cement surface is lost. Therefore, the effect of fineness on strength observed in this work would probably have been greater if a finer sand had been used in the tests instead of standard Ottawa sand.

It is unexpected that, with both Ls_2 and Ls_1 clinkers in the t-state of seasoning, the former, though ground nearly one and one-half times as fine as Ls_1, required about the same water for consistency as the latter (Tables VI and IX). Probably

TABLE X. EFFECT OF ADDITIONS TO t-SEASONED CLINKER

1.5% Addition	Water for Normal Consistency	Initial Set		Tensile Strength 3-day	Tensile Strength 7-day
	%	*Hr.*	*Min.*	*Lb./sq. in.*	*Lb./sq. in.*
	Clinker *Ua*				
None	22.5	1	50	275	344
Gypsum	22.5	2	20	314	418
Plaster	21.0	0	20	324	451
$CaCl_2$	18.0 (15.5)	1	00	380	408
	Clinker *Pd*				
None	21.0	1	50	308	416
Gypsum	21.0	2	10	378	510
Plaster	21.5	0	30	381	457
$CaCl_2$	19.5 (17.5)	1	10	408	500
	Clinker *Ha*				
None	22.5	2	50	268	379
Gypsum	22.5	2	30	325	424
Plaster	21.5	0	20	326	392
$CaCl_2$	19.5 (17.5)	0	50	356	421

TABLE XI. EFFECT OF CARBON DIOXIDE ON t-SEASONED CLINKER CONTAINING 1.0 PER CENT CALCIUM CHLORIDE

Clinker	Before CO_2 Water for N. C.	Before CO_2 Initial set		After CO_2 Water for N. C.	After CO_2 Initial set	
	%	*Hr.*	*Min.*	%	*Hr.*	*Min.*
Ua	19.0	1	40	26.0 (23.0)	0	20
Pd	20.0	1	10	24.5 (23.5)	2	00
Ha	20.0	1	40	22.5	1	50
Ls_2	19.0	1	20	28.0 (24.0)	0	00

this is connected with change in mineral size distribution, particularly with a relatively greater surface evolution of $3CaO{\cdot}SiO_2$ (*9*), the constituent responsible for slow setting (*15*). Similarly the relatively low requirement of water for normal consistency in the case of t-clinker *Pd* (Table VI) is probably due to its relatively high $3CaO{\cdot}SiO_2$ content (computed in Table I). These results indicate the unexpected possibilities of seasoning as related to fineness. It would seem desirable to reinvestigate on a rational basis of proper seasoning the subjects of strength, permeability, durability, and other properties as related to fineness.

TABLE XII. STRENGTH OF COMMERCIAL CEMENTS

Fineness Sq. cm./gram	Water for N. C. %	—Tensile Strength— 3-day Lb./sq. in.	7-day Lb./sq. in.
1680	22.5	291	368
1760	22.5	305	380
1840	25.0	289	335

For a long time it has been recognized that excess quantities of gypsum are deleterious to cement, so that specifications limit the amount that may be present to 2 per cent sulfur trioxide. In contact with sea water the presence of calcium sulfate in cement appears to be especially unfavorable (cf. *2*, *7*, *8*). Hence under more severe conditions it may be considered desirable to reduce by proper seasoning the gypsum content to lower amounts than are commonly employed today.

In hot climates difficulties of quick setting, or of reversion to quick setting on storage, are increased (*14*). Inasmuch as Portland cement is apparently most stable as regards setting when it is in the t-state of seasoning, thoroughly seasoned cements might be used to advantage in unfavorable climates.

Besides activation of tricalcium silicate and tricalcium aluminate, exposure to steam also will slake any free lime that may be present. Slaking, of course, is always desirable and under certain conditions of too high free lime is indispensable.

Absorption of water vapor by cement is exothermic, as is evident from the temperature rise on absorption of steam by fresh cement. Further, cements in the t-state of seasoning require a minimum of mixing water for consistency. Well-seasoned cements, therefore, would be expected to show a lower heat effect during setting and hardening. This property would have value in mass concrete construction.

Shrinkage of cement during hardening commonly decreases with decrease in the amount of mixing water. Hence it may be expected that cement which is thoroughly seasoned and therefore requires a minimum of mixing water would show the least shrinkage.

In brief, it appears that controlled seasoning at elevated temperatures offers the advantages of a uniform product, of placing the cement in a condition of optimum strength, of permitting the practical production of fine cement of high strength, of permitting a reduction in gypsum content, of promoting the utilization in hot climates and possibly also the utilization in saline water, of slaking free lime, and of reducing the heat evolution and shrinkage during hardening.

Plant conditions for a seasoning process are favorable. Heat is already stored in the clinker both because it is retained from burning and is liberated in crushing and grinding. Similarly, waste steam is readily available. The main requisites are satisfactory exposure of the cement at properly controlled temperatures. Judging from the literature (*1*), the all-important condition of controlled temperature which is necessary to avoid overseasoning appears to have been overlooked in the past. Although other factors may have intervened, probably this oversight largely accounts for the apparent relinquishment of previous cement seasoning processes.

Acknowledgment

Acknowledgment is made to F. P. Bliss for chemical analysis of the clinkers and for assistance in the tests.

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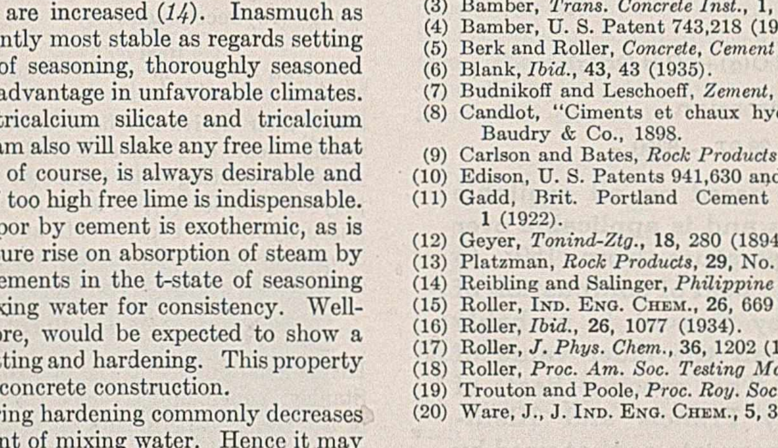

DRYING CRUDE RUBBER AFTER WASHING

Courtesy, Firestone Tire and Rubber Company

Free Energy of Ethylene Hydration

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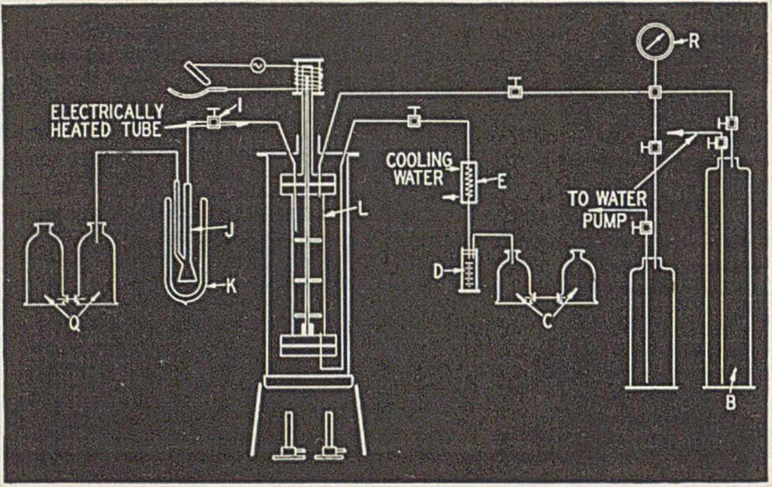

FIGURE 1. DIAGRAM OF APPARATUS

Within an accuracy of ±500 calories, the free energy change for the hydration of ethylene,

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

is given by the expression,

$$\Delta F° = 26.9T - 8300$$

This equation is based on all available experimental data and is applicable over a range of temperature from 150° to 380° C. The newer heat of combustion of ethanol offered by Rossini is probably more accurate than the older value of 328,700 calories. The specific heat of ethylene used by Francis and Kleinschmidt is not as accurate as that used by Parks and Huffman.

THERE is a considerable discrepancy between the free-energy change of hydration of ethylene as predicted from existing thermodynamic data and that calculated from the two existing experimental determinations. Using available data on free energy of formation, Parks and Huffman (*10*) compute the expression,

$$\Delta F° = -4350 + 26.1T$$

for the gas-phase hydration of ethylene. Because of a more recent determination of the heat of combustion of alcohol (*12*), they suggest that the equation might better be

$$\Delta F° = -6350 + 26.1T$$

Because of inaccuracies in the data on heat of combustion of ethylene, their recommended free-energy equation is probably accurate only to ±2000 calories. Francis and Kleinschmidt (*3*) give an equation for hydration with liquid water, which, combined with an equation for the free energy of vaporization of water based on Keenan's tables (*5*), gives

$$\Delta F° = -12{,}140 + 39.2T$$

This equation indicates a greater free-energy temperature coefficient than that of Parks and Huffman, chiefly because of the difference in the specific heat of ethylene gas.

On the basis of an experimental determination of the vapor-phase equilibrium of the hydration of ethylene using an alumina catalyst at 69.6 atmospheres and 380° C., Saunders and Dodge (*13*) recommend

$$\log_{10} Kp = \frac{1090}{T} - 4.71 \log_{10} T + 0.00235T + 7.05$$

Since their derivation used existing thermal data and the specific heats of Parks and Huffman, their formula offers no check on existing data except at the temperature they employed. Bowles (*1*), as a result of a series of batch liquid-phase hydration experiments at temperatures from 225° to 325° C. and a pressure of 400 atmospheres, using dilute mineral acids as catalysts, recommends the expression

$$\Delta F° = -10{,}120 + 30.2T$$

His calculations made use of hydrocarbon vapor fugacities. Stanley, Youell, and Dymock (*14*) have published the results of a series of experiments in which they studied the vapor-phase hydration reaction, approaching equilibrium from both sides at atmospheric pressure and temperatures from 145° C. to 250° C., recommending

$$\log_{10} Kp = \frac{2100}{T} - 6.195$$

Other published data, including those of Swann, Snow, and Keyes (*15*) and Kleaver and Glaser (*6*), have not yielded results suitable for free-energy determinations.

Apparatus

The copper-lined steel reactor, *L* (Figure 1), was 14.25 inches (36.2 cm.) long, with a capacity of 346 cc. The contents were agitated by three disks operated by a solenoid, and the reactor was maintained at constant temperature by a vapor bath. There was a bottom opening for withdrawal of liquid-phase samples, one 5.5 inches (14 cm.) from the top for vapor-phase samples, and one at the top for maintenance of constancy of pressure during sampling.

Vapor-phase sampling was accomplished through an electrically heated line and valve, *I*, preventing condensation prior to pressure reduction. Four thermocouples were provided to insure maintenance of the necessary temperature. A glass condenser, *J*, cooled by ice water in a Dewar flask, *K*, was used to remove ethanol and water vapor; gas-measuring bottles, *Q*, collected the

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noncondensed gases. Flashing of ethanol from the liquid-phase sample was prevented by withdrawing it through a cooler, *E*, whence the sample passed to a separator, *D*, where ethylene was removed and measured in bottles, *C*. Pressure was maintained in the reactor by connecting it to an 11-liter high-pressure storage vessel, *B*, in which the ethylene gas was stored. A Bourdon gage, *R*, calibrated against a "dead-weight" gage, was used for pressure measurements.

The ethylene used was the medical grade and analyzed better than 99.5 per cent ethylene.

Experimental Procedure

Seven runs at a constant temperature and four different pressures were made, and a second series at a constant pressure but four different temperatures varying from 176° to 307° C. The catalyst was sulfuric acid averaging about 3 mole per cent.

In each run liquid-phase samples were withdrawn at intervals (approximately half-hour) and analyzed for ethanol. When the concentration became constant, a vapor sample was removed. The final liquid-phase sample was analyzed for ethylene, ethanol, and sulfuric acid. The ethylene was determined by measuring the volume of gas which flashed on pressure reduction and the ethanol by the method of Pondorf (*11*), which was found to be rapid and satisfactory. In analysis of the gas phase, the total condensate was weighed and analyzed for ethanol, and the ethylene determined by measuring the volume and composition of noncondensed gas.

Discussion of Results

The results of these determinations are presented in Table I. From the vapor-phase equilibrium data the free energy of hydration was calculated for each run,

$$\Delta F^\circ = -RT \ln \frac{(yf_\pi)_{C_2H_5OH}}{(yf_\pi)_{C_2H_4}\,(yf_\pi)_{H_2O}}$$

Data are not available for the evaluation of the fugacities of water and ethanol at pressures above the vapor pressure and at temperatures below the critical. For this reason it was necessary to resort to the use of fugacity data for hydrocarbon vapors (*2*, *7*, *8*, *9*) based on equivalent conditions of reduced temperature and pressure. Calculations were made to check this method in regions where actual data were available. The following is a comparison of fugacity of saturated vapors based on hydrocarbon vapor data with that calculated from actual data (*4*, *5*):

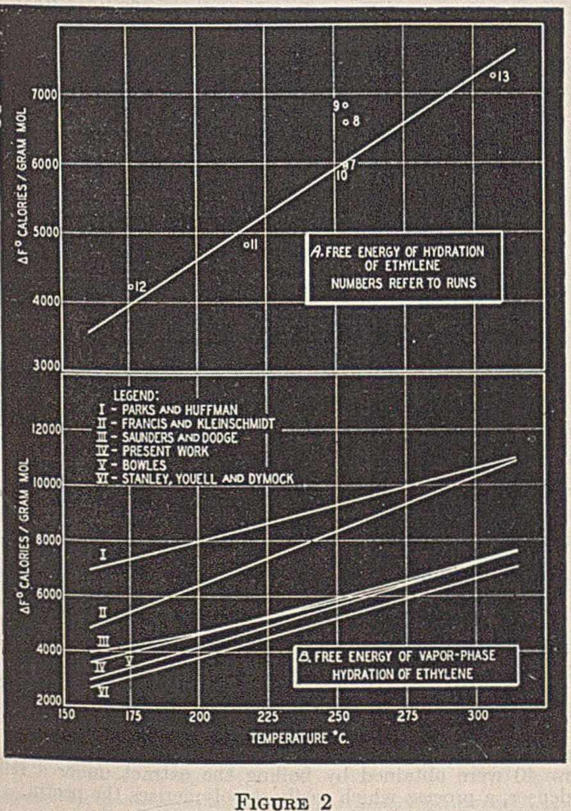
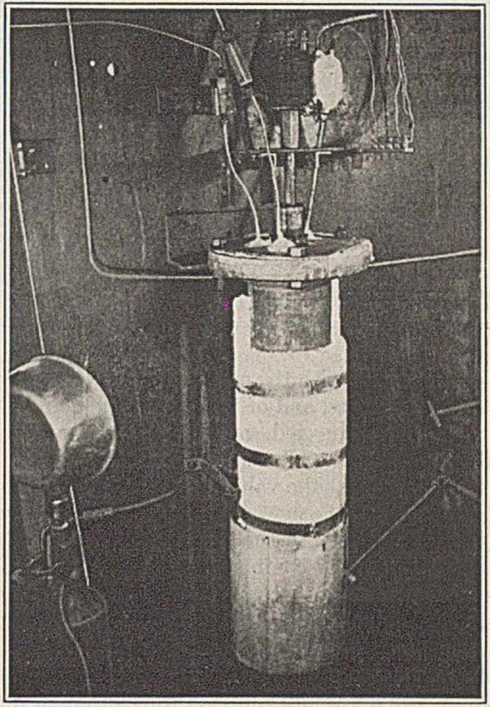


FIGURE 2



ASSEMBLED APPARATUS

Temp.	$(f_p)_{C_2H_5OH}$ True	$(f_p)_{C_2H_5OH}$ Calcd.	Error	$(f_p)_{H_2O}$ True	$(f_p)_{H_2O}$ Calcd.	Error
° *C.*	*Atm.*	*Atm.*	%	*Atm.*	*Atm.*	%
170	14.0	13.21	− 5.6	6.80	7.42	+9.1
200	24.0	22.6	− 5.8	13.90	14.22	+2.3
243.1	46.5	41.1	−11.2	30.0	30.7	+2.3

It is worthy of note that the use of pressures in place of fugacities produces relatively slight changes in the calculated ΔF°. This fact is not surprising when it is noted that under the conditions of the experiments, ethylene existed at such high reduced temperatures that its behavior approached that of a perfect gas. Whereas the ethanol and water existed at far lower reduced temperatures, their deviations from perfect gas behavior tend to cancel, since they occur in the free-energy equation as a ratio. At a pressure of 200 atmospheres the value of ΔF° calculated with pressures deviates about 10 per cent from the value calculated with fugacities.

Figure 2*A* is a plot of the experimentally determined values of the free energy of hydration for the reaction,

$$C_2H_4(g) + H_2O(g) \longrightarrow C_2H_5OH(g)$$

The recommended equation based on this plot is

$$\Delta F^\circ = -7780 + 26.2T$$

Two side reactions were found to occur appreciably under favorable conditions. Above 250° C. and 200 atmospheres, polymerization of ethylene was found to be considerable, when using approximately 3 mole per cent sulfuric acid catalyst. At temperatures below 220° C. ether formation was very noticeable.

In Figure 2*B* the equations for free energy of hydration recommended by previous investigators have been plotted with the present equation. The results of the present investi-

Table I. Equilibrium Composition

Run No.	Temp. ° K.	Pressure Atm.	Mole Fraction in Liquid Phase EtOH	C_2H_4	H_2SO_4	H_2O	Mole Fraction in Gas Phase EtOH	C_2H_4	H_2O
4	527	264.2	0.0755	....	...	0.885	...	...	....
5	527	196.9	0.063	0.0115	0.023	0.903	...	...	....
6	527	129.7	0.046	0.0076	0.017	0.929	...	...	....
7	527	82.6	0.014	0.0023	0.028	0.956	0.076	0.475	0.449
8	527	196.9	0.060	0.0079	0.014	0.918	0.104	0.380	0.516
9	527	264.2	0.084	0.0197	0.015	0.881	0.075	0.250	0.675
10	527	129.7	0.0445	0.0075	0.011	0.937	0.095	0.226	0.679
11	491	196.9	0.055	0.0110	0.033	0.901	0.226	0.225	0.385[a]
12	449	196.9	0.039	0.0093	0.032	0.920	0.083	0.475	0.442
13	580	197.8	0.028	0.0170	0.002	0.953	0.033	0.394	0.573

[a] Remaining fraction, ether.

gation correlate well with the experimental work of Saunders and Dodge, of Bowles, and of Stanley, Youell, and Dymock. In contrast, the computed values of Parks and Huffman and of Francis and Kleinschmidt indicate far higher values. The fact that the values of $\Delta F°$ calculated by Parks and Huffman, using the newer heat of combustion of ethanol, are 2000 calories closer to the experimental values indicates that the newer heat of combustion of ethanol (326,610 calories) is probably more accurate. Although the curve of Francis and Kleinschmidt is higher than the experimental curves at the higher temperatures, because of its greater slope it intersects the extrapolated experimental curves at about 25° C. This would indicate that although the $\Delta F°_{298}$ used by Francis and Kleinschmidt is accurate, their specific heat data used in obtaining $\Delta F°$ as a function of temperature were in error. Accordingly, it is probable that the specific heat equation used by Parks and Huffman is the more reliable.

An expression for the vapor-phase hydration that satisfactorily correlates all available data (including the present work) is given by the equation,

$$\Delta F° = 26.9T - 8300$$

The close agreement of the experimental data indicates that this expression is probably accurate within ±500 calories.

The fact that liquid-phase concentrations of ethanol as high as 18 weight per cent of alcohol were attained in the experiments indicates that the direct hydration of ethylene may well have industrial possibilities. If dilute sulfuric acid catalysts are to be used, it is apparent that the temperature must lie between 220° and 250° C. in order to avoid side reactions to ether or polymerized ethylene. On the other hand, the temperature should be as near 250° C. as possible to secure increased reaction rate.

Nomenclature

$\Delta F°$ = standard free-energy change
f_p = fugacity of satd. vapor at temp. in question
f_π = fugacity of pure gas at temp. in question at pressure equal to total pressure
(g) = gas phase
Kp = equilibrium constant expressed with pressures in atmospheres
R = gas constant
T = temp., ° K.
x = mole fraction of substance in liquid phase
y = mole fraction of substance in vapor phase

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CRANBERRY PECTIN PROPERTIES

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THE cranberry is interesting to jelly workers on account of the high viscosity of solutions made from its extracted pectin. It is also interesting because of the formation of jellies of low sugar content. The reason for the formation of low-sugar jellies lies in the low pH of the fruit extract and in the quality and quantity of the pectin present. Attempts to make 65 per cent sugar jellies from the extracted juice have failed. If the pectin present in the extract is precipitated with alcohol to get rid of excess acid and is then put back into water solution, jellies containing 65 per cent sugar can be made with ease. It seemed desirable for a better understanding of the fundamentals of jelly making to investigate properties of precipitated cranberry pectin and its relationship to alcohol-precipitated apple and lemon pectins.

Jelly from Heat-Extracted Juice

In the course of the preparation of cranberry pectin a correlation was found between the viscosity of heat-extracted cranberry juice and the strength of jelly produced from these extracts.

The cranberries used were purchased in the local market without regard to variety at intervals from October through January. The juice for the jelly strength–viscosity correlation was extracted by boiling the cranberries with an equal weight of water in a covered dish until the berries were soft. The boiling period approximated 10 minutes. The juice was pressed out of the pulp through muslin cloth and then filtered through flannel. Viscosities of the extracted juice were measured at 26° C. with a large capillary Ostwald viscometer. The relative viscosities of the juice varied from 132 to 15. Contrary to expectation the early season extractions had relative viscosities of from 40 to 60, while the extract with a relative viscosity of 132 was obtained from berries purchased in December. Relative viscosities below 40 were obtained by boiling the extract under a reflux condenser, a process which easily depolymerizes the pectin.

Jellies made from the heat-extracted juice of the cranberry show a definite correlation between jelly strength and viscosity of extracted juice. Maximum strength of jellies appear between 38 and 41 per cent of sugar. The viscosity of 0.5 per cent solutions of cranberry pectin is an index to its sugar-supporting capacity. This index of sugar-supporting capacity is in closer agreement to apple pectin solution requirements than to solutions of lemon pectin. Differences are thought to be due partly to fruit salts present.

Jellies were made by weighing out a sugar portion and then adding the extracted cranberry juice until the combined weight was 100 grams. This sugar-juice mix was heated, with stirring, just to boiling and then poured into a standard 6-ounce jelly glass. The jelly was allowed to set at room temperature until cool and then placed in a constant-temperature oven at 26° C. Twenty-four hours after the pouring time the jelly was turned out of the glass onto a flat dish and the jelly strength measured on the bottom surface with the Tarr-Baker jelly strength tester (*12*). Data obtained are given in Table I.

Maximum jelly strengths were obtained at all viscosities where the sugar–cranberry juice ratio was 40 to 60.

Viscosity–Jelly Strength Correlation

When plotted, the data in Table I produced a series of curves as shown in Figure 1. The jelly strength corresponding to the peak of each curve plotted against the $\log_{10}$ of the viscosity produces a straight line as in Figure 2. The optimum jelly strengths taken are as follows:

Relative viscosity, 26° C.	132	54	45	40	29	24	15
Jelly strength, 26° C.	240	175	150	140	130	100	65

The maximum strength, x, for a jelly as made in the foregoing experiment from an extracted cranberry juice of viscosity y may be expressed by the formula, $\log y = 0.0052x + 0.86$ for the line in Figure 2.

All the curves in Figure 1 reach a peak at approximately the proportion of 40 grams of sugar to 60 grams of juice. Below a sugar content of 30 per cent only sirups are formed. Above 60 per cent sugar a pectin precipitate forms on the surface. An increasing amount of pectin precipitation is apparent after the 40 per cent sugar concentration is passed. The explanation for the complete precipitation above 60 per cent sugar probably lies in the fact that there is only 0.12 per cent of a very high-grade pectin present, and at this high sugar concentration, coincident with the high hydrogen-ion concentration of the cranberry juice, this small amount of pectin present is easily precipitated. A larger amount of a low-grade pectin would be only partially precipitated under similar heat treatment. An extended period of boiling would completely precipitate even large amounts of low-grade pectin under similar conditions. This action of premature precipitation or gelatin is in agreement with Olsen (*10*). Cox (*2*) also explains the failure of an attempt to make cranberry jelly with the usual 65 per cent sugar concentration as due to pre-gelation. The rate of dehydration of the pectin particle is rapid at this high sugar concentration under normal circumstances. The rate of dehydration and precipitation is increased as the hydrogen-ion concentration is increased.

Table I. Strength of Jellies Made from Cranberry Extracts

Sugar	Juice	Jelly Strength at Viscosity of:						
		132	54	45	40	29	24	15
Grams	*Grams*	*Cm. of water pressure*						
30	70	66	...	1	...	...	...	..
35	65	220	140	115	110	90	38	10
40	60	230	170	140	138	130	100	65
45	55	185	100	55	80	80	70	50
50	50	47	30	20	8	23	18	2
55	45	...	...	1	...	...	2	..

All of the jellies produced around a 40 per cent sugar concentration were very elastic and attractive in appearance. The pectin present must be of high grade, since the jelly produced from the extract with a viscosity of 132 contained only 0.18 per cent of pectin and gave a strength of 230. Either a large quantity of low-grade or a small amount of high-grade pectin is necessary to produce such strength.

Cranberry Pectin Extraction

In order to produce jellies from cranberry pectin containing 60 per cent sugar, it was necessary to precipitate the cranberry juice extract with alcohol:

The juice from 800 grams of cranberries was extracted by boiling with an equal weight of water for 10 minutes. The extracted juice was pressed from the pulp through a muslin cloth and then clarified with the aid of Filter-Cel by filtering through paper on a Büchner funnel. The filtrate was precipitated in twice its volume of 90 per cent alcohol, filtered on silk, and washed with 95 per cent alcohol and then with ether, squeezing as dry as possible after each washing. The pectin was dried at 60° C. for 20 hours. The pulp from the first extraction was extracted a second time by boiling with 800 grams of water. The extract was pressed out and clarified, and the pectin was precipitated, washed, and dried as with the first extraction. The first extraction yielded 2.38 grams or 0.30 per cent pectin and the second 1.36 grams or 0.17 per cent pectin. A 0.25 per cent solution of the pectin from the first extraction had a relative viscosity of 53.7 at 26° C., the highest viscosity of a pectin solution on record. A 0.5 per cent solution of this first extraction could not be measured with the Ostwald viscometer. A 0.5 per cent solution of the pectin from the second extraction had a relative viscosity of 79.0.

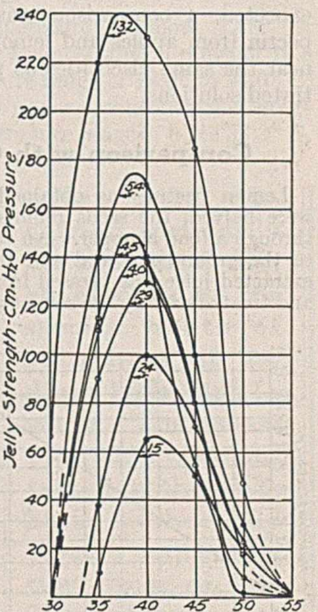

Figure 1. Jelly Strength Curves for Cranberry Extracts of Varying Viscosity (Viscosity Values on Curves)

Viscosity–Jelly Strength Relationships of Cranberry Pectin

Viscosities of fruit juice extracts for jelly purposes and viscosities of similarly extracted lemon pectins are an index of their sugar-supporting capacity for a given jelly strength (*1*, *6*). In order to see if this relationship will hold with the cranberry pectin, a 0.5 per cent solution of the second extraction described above was heated to boiling in an oil bath under a reflux condenser. After 15 minutes the relative viscosity had dropped from 79 to 38.5. A 50-gram sample was taken and the refluxing continued until samples were obtained at relative viscosities of 26.3, 14.8, and 10.6. Sixty per cent added sugar jellies were made up by adding the proportionate sugar requirement, x, given by the formula, $\log y = 0.833\,x + 0.195$, found to produce jellies of strength 40 (cm. of water pressure) from apple juice extracted at 100° C. for jelly purposes. Each mix was boiled to a point 2 grams beyond a 60 per cent concentration of added sugar, poured into a 6-ounce jelly glass containing 2 cc. of 12.5 per cent citric acid (a procedure similar to Olsen's excess acid method, *9*), and covered immediately. The jellies were allowed to set at room temperature until cool and then held at 26° C. Twenty-four hours after pouring time a jelly strength measurement was made on their upper surface. The data on these cranberry pectin jellies are presented in Table II.

TABLE II. JELLIES FROM DIFFERENT VISCOSITY BUT EQUALLY CONCENTRATED SOLUTIONS OF CRANBERRY PECTIN

Relative Viscosity, 26° C.	0.5% Pectin Soln.	Sugar Added	Water Added	Final Weight, Including 2 Cc. 12.5% Citric Acid	Jelly Strength
	Grams	*Grams*	*Grams*	*Grams*	*Cm. H_2O pressure*
38.5	50	83.5	15	139.0	40
26.3	50	73.5	5	122.5	44
14.8	50	58.5	..	97.5	48
10.6	100	98.4	..	164.0	47

Since these jellies gave approximately the strength values expected, a comparison was made of similarly extracted pectin from apples and lemons with cranberry pectin at as near the same viscosities as possible and in equally concentrated solutions.

Comparison with Other Fruit Pectins

Lemon pectin was obtained from fresh fruit. The lemons were halved, the seeds removed, and the pulp and skins put through a food chopper. An equal quantity of water was added to the ground material and then boiled for 45 minutes. The extracted juice was pressed from the pulp through muslin cloth and treated exactly the same as in the cranberry pectin recovery. A 0.5 per cent solution of this lemon pectin had a relative viscosity of 15.4 at 26° C.

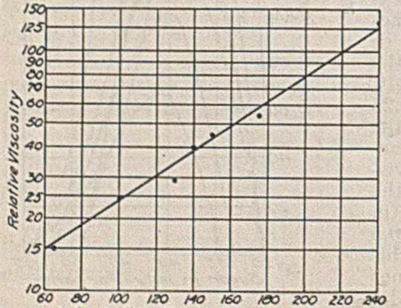

FIGURE 2. LOGARITHMIC RELATIONSHIP OF VISCOSITY OF EXTRACT TO OPTIMUM STRENGTH OF CRANBERRY JELLY

Apple pectin was extracted from ripe Stayman apples by boiling the sliced apples with half their weight of water for 15 minutes. The extracted juice was handled in the same way as the lemons and cranberries except that the starch present after clarification was hydrolyzed with a diastatic enzyme preparation, and after hydrolysis the extract was reclarified with Filter-Cel. The apple pectin prepared in this manner had a relative viscosity at 26° C. of 30.7.

One-half per cent solutions of the first-extraction cranberry pectin and the apple pectin were boiled under a reflux condenser to the viscosities shown in Table III. An attempt was made to regulate hydrolysis of these pectin solutions to a viscosity comparable to the value found for a 0.5 per cent solution of the lemon pectin, in order to compare the three pectins on the same basis of viscosity and concentration of solution. Sixty per cent sugar jellies were made according to the proportionate sugar requirement shown by formula at the pH values given in Table III. Jelly strength measurements were made at 26° C. after a 24-hour setting period.

TABLE III. STRENGTH OF JELLIES PRODUCED FROM 0.5 PER CENT SOLUTIONS OF LEMON, APPLE, AND CRANBERRY PECTINS PREVIOUSLY ADJUSTED TO SIMILAR VISCOSITIES

pH of Jelly	Lemon, Viscosity = 15.4, Initial pH = 3.51	Apple, Viscosity = 17.2, Initial pH = 3.35	1st Cranberry, Viscosity = 16.4, Initial pH = 3.13	2nd Cranberry, Viscosity = 14.8, Initial pH = 3.41
3.10	...	23	15	..
2.90	129	43	31	..
2.70	88	50	35	..
2.50	80	43	31	48

The difference in jelly strength values of the jellies made according to calculated sugar requirement for the three pectins is considerable, especially between the lemon jelly values and those of the other two. The difference in strength between the apple and the first-extraction cranberry pectins is not great, and the type of curve for jelly strength against pH would be similar. The conclusion cannot be drawn from the data that lemon pectins are of higher grade than apple and cranberry pectins, because it must be remembered that the apple and cranberry pectins underwent a hydrolysis in addition to regular extraction procedure. Precipitation after hydrolysis should have been carried out.

Olsen (*10*) has pointed out that there are distinct differences in jelly characteristics, especially in elasticity properties, between apple and lemon pectins. If the apple jellies were of equal strength to the lemon jellies, these differences in characteristic physical properties would be more apparent. In the present instance the lemon jellies, although of much greater strength, appear as elastic as the apple jellies. Comparing the cranberry jellies it will be noted that the first extraction produces a lower strength jelly than the second extraction (the data for the second extraction are introduced from Table II into Table III for comparative purposes) whereas the jelly from the second extraction compares favorably with the apple pectin jelly of pH 2.7. Olsen (*9*) has shown that the excess acid method produces a jelly with a strength equal to that of the optimum pH jelly by the short boil method. Therefore, the excess acid cranberry pectin jelly with an approximate pH of 2.5 may be compared with the apple jelly of strength 50, even though it is not made by the same method.

Reason for Strength Differences

The differences in jelly strength between the jellies from the first and second cranberry extractions may be due to the fruit salts present. According to Morse (*4*) there is 0.158 per cent ash in the cranberry. The main constituent of this ash is potassium oxide, present as 0.068 per cent of the berry. Fellers (*3*) gives the acids present as 2.4 per cent. Eighty-eight per cent of the fixed acids is citric according to Nelson (*8*). In the first extraction a large portion of the potassium citrate is removed owing to easy solubility in water, and even though it is present in very small amounts it will be precipitated and occluded along with the pectin because of its low solubility in alcohol. In the second extraction a much smaller portion of the salt would be present.

From the trend of the data on salt effect by Myers and Baker (*5*), it may be assumed that at pH values below 3.35 the addition of a slight amount of salt will bring about a decrease in strength of jellies. The lower the pH the more rapid will be this decrease for a like amount of salt. In the comparison of the strength of jellies made up at the same pH from the first and second extractions from the cranberries, it may be said that the total cation concentration is higher in the first extraction, and that coagulation and precipitation or pregelation tendencies are greater. Therefore, the strength of the jelly would be lower. According to Spencer (*11*) a sodium salt decreases the jelly field on the acid side. It may be assumed that the jelly strength would be similarly affected by the potassium salt. It is well known that potassium acid tartrate has this effect on the formation of jelly from juice extracted from overripe grapes.

The differences in jelly strength between the jellies from the lemon and the cranberry pectins may be partly due to the differences in actual pectin present. A determination showed 75.76 and 69.28 per cent pectic acid present in the 0.5 per cent solutions of the lemon and cranberry pectins, respectively. This difference in pectic acid is not considered as important in jelly formation as the degree of polymerization of the galacturonic acid (*7*).

The relative concentrations of basic ions (calcium, magnesium, potassium, sodium) in the pectin from the lemon and the cranberry may account for part of the variations in jelly strength of jellies from the two sources. This phase was not within the scope of the investigation. Consequently, analysis of the pectin ash which would bring out these relationships was not made.

Acknowledgment

The pH measurements were made by G. M. Gilligan.

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Specific Heats of Sodium Hydroxide Solutions

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HEAT balance calculations of processes involving the mixing, diluting, or concentrating of solutions must be based on the specific heats and heats of dilution of the solutions. It has been shown (*4*) that such thermal data are conveniently assembled in the form of an enthalpy-concentration diagram, or Merkel chart (*5*), from which items for heat balances are readily taken.

When, however, the construction of enthalpy-concentration charts for common commercial chemicals is attempted, it is soon found that the necessary thermal data are usually lacking. As a start towards remedying this lack of data, this paper presents new experimental results on the specific heats of sodium hydroxide solutions over a concentration range of 4.08 to 51.15 per cent of sodium hydroxide by weight, and a temperature range of 3.1° to 88.5° C. (37.5° to 191.3° F.). When combined with data on heats of dilution, which have been presented in another paper (*1*), the new data allow the construction of an enthalpy-concentration chart over the same ranges of concentration and temperature.

The work was done entirely from a practical point of view. No attempt is made to develop or test theories of solutions or to present the data on any but an empirical basis. Extreme accuracy was not expected, but the results are believed to be of adequate precision for all engineering applications.

Previous Work

Specific heats of sodium hydroxide solutions were reported by Thomsen (*13*) over a concentration range of 1.1 to 23 per cent and at an average temperature of about 17.5° C. (63.5° F.); by Tucker (*14*) over a concentration range of 16.5 to 47.4 per cent and a temperature range of 18.9° to 24.0° C. (66.0° to 75.2° F.); by Pratt (*6*) over a concentration range of 0.6 to 16 per cent and a temperature range of 0° to 33.3° C. (32° to 92° F.); by Richards and associates (*7–11*) over a concentration range of 0.139 to 27.8 per cent and a temperature range of 15° to 20° C. (59° to 68° F.); and by Gucker and Schminke (*3*) over a concentration range of 0.158 to 8.157 per cent at a temperature of 25° C. (77° F.).

Experimental Procedure

The adiabatic method developed by Richards (*11*) was used. The calorimeter proper, surrounded by a "submarine" was totally immersed in a bath; the temperature of the bath

New data, obtained primarily for industrial use, are reported on the specific heats of solutions of sodium hydroxide in water. The measurements were obtained by the adiabatic method and cover a concentration range of 4 to 51 weight per cent sodium hydroxide and a temperature range of 37° to 191° F.

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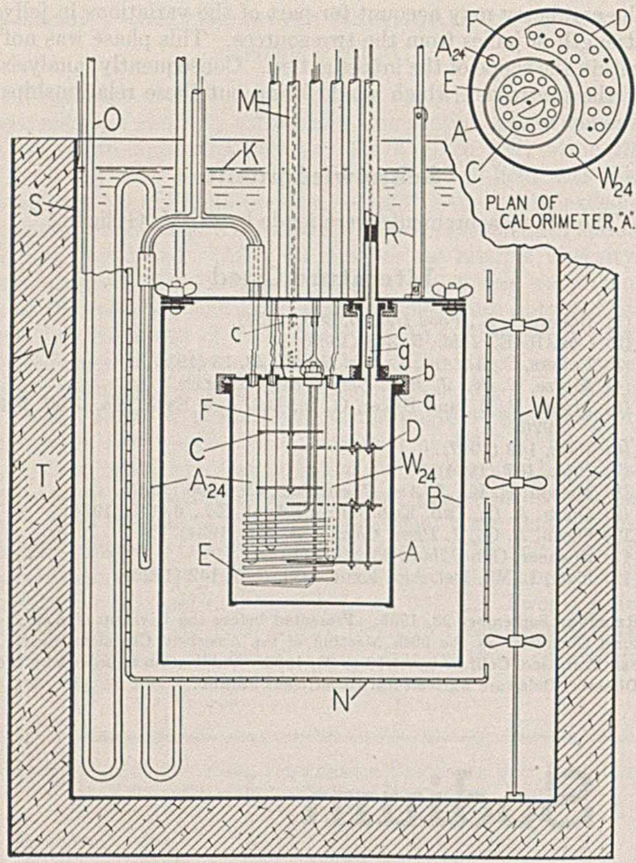

FIGURE 1. WORKING CALORIMETER

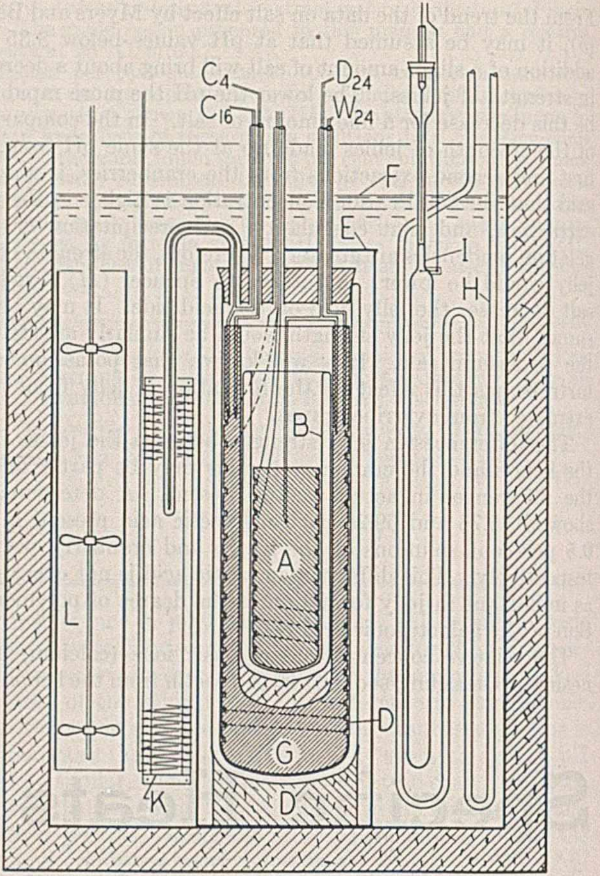

FIGURE 2. COLD CALORIMETER

was maintained, as nearly as possible, equal to that of the calorimeter. The heat input was determined by measuring the voltage and current of an electric heater and the time of heating. Corrections for heat of stirring were found by measuring the temperature drifts before and after the heating period.

Apparatus

The calorimeter was so designed that with a slight modification it was possible to measure either specific heats or heats of dilution. All parts which came in contact with the solutions were of pure nickel. All thermoelements were of No. 40 copper and No. 30 constantan wires and were constructed and used according to the recommendations of White (*15*).

Figure 1 is a diagram of the calorimeter:

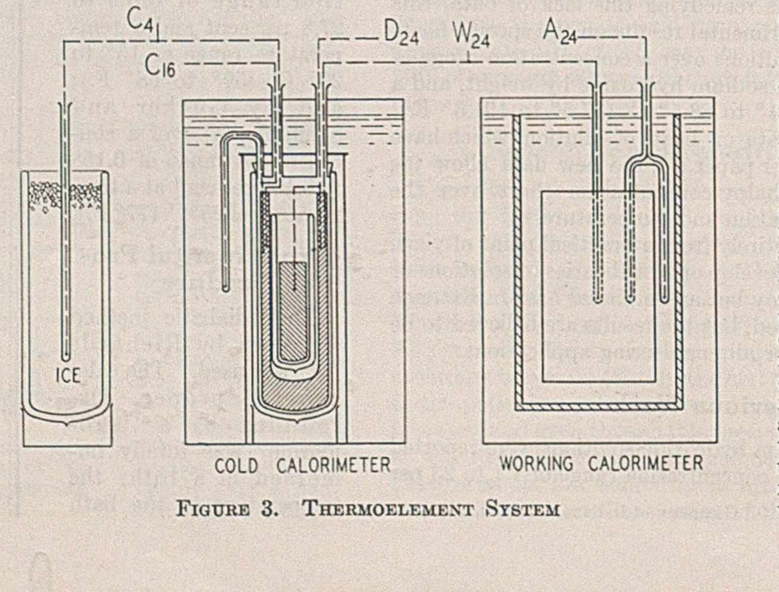

FIGURE 3. THERMOELEMENT SYSTEM

> Vessel *A* has a capacity of about 650 cc. (22 fluid ounces) and contains the solution undergoing investigation. The cover is fastened to the flange, *a*, by means of the follower ring, *b*. It is suspended from the cover of a "submarine" vessel, *B*, by Formica hangers, *c*, providing a 4-cm. (1.6-inch) air space between the submarine and the calorimeter. The submarine is completely immersed in a bath, *K*, which is contained in the inner can, *S*. Can *S* is lagged by 1 inch of felt, *T*, which, in turn, is inside outer can *V*. Reciprocating stirrers, *C* and *D*, were operated at a rate of sixty double strokes per minute. Each stirrer had a short Formica section, *g*, to reduce heat conduction. Chimneys are shown at *M*. The quantitative heating element, *E*, was similar in design to that used by Gucker and Schminke (*3*). An auxiliary heating element, *F*, was used to bring the calorimeter rapidly to temperature when operating at elevated temperatures, and heating coil *O* could be used to heat the bath rapidly to the working temperature. Adiabatic control to within ±0.02° F. was made possible through use of a differential thermoelement of twenty-four pairs of wires, A_{24}, directly connected to a sensitive galvanometer, and the use of electrolytic heating (*1A*, *2*). The thermoelement junctions were insulated by a mixture of ultramarine and collodion, and were immersed in mercury to reduce lag. In connection with electrolytic heating it was found that when the submarine itself was used as an electrode, true adiabatic conditions did not prevail when the adiabatic bath thermoelement indicated zero temperature difference. The submarine was actually slightly warmer than bath *K*. This difficulty was overcome by surrounding the submarine with a coarse metal grid, *N*, separated from the wall by a distance of 1.5 cm. (0.59 inch) and using this grid and inner can *S* as electrodes. The current through coil *E* was determined by measuring the voltage across a standard

one-ohm resistance. A Leeds and Northrup type K-2 potentiometer was used in all voltage measurements. A period of 600 seconds was used for heating, and the time was measured with a precision of better than 0.01 per cent by means of a pendulum clock and automatic switch.

The temperature change of the solution was measured by means of a twenty-four-junction thermoelement, W_{24}. This thermoelement and one of four junctions, to be referred to later, were calibrated by comparison with a platinum resistance thermometer which had been calibrated to ±0.02° F. in this laboratory at the ice point, steam point, sulfur point, and the transition point of $Na_2SO_4 \cdot 10H_2O$.

In order to maintain all potentiometer readings in the lowest range where the sensitivity is 0.1 microvolt, the "cold" junctions of thermoelement W_{24} were maintained at a constant temperature above 32° F. by means of a cascade cold calorimeter suggested by White (*16*). This calorimeter is shown in Figure 2, and Figure 3 shows diagrammatically the thermoelement system:

Copper block *A* (Figure 2) is contained in a small vacuum flask, *B*. Flask *B* is placed inside a hollow copper block, *G*, which in turn is placed inside a wide-mouthed 1-liter vacuum flask, *D*. This vacuum flask is incased in a sheet iron vessel, *E*, which is, in turn, immersed in a thermostatically controlled bath, *F*. Each copper block is provided with a resistance heater, and current can be passed through these resistances individually or in series. A sixteen-junction thermoelement, C_{16}, similar to the twenty-four-junction element of the adiabatic control, measures the temperature difference between the outer block and the bath. A four-junction thermoelement, C_4, with one set of junctions in an ice bath, measures the temperature of the outer block. A twenty-four-junction thermoelement, D_{24}, measures the temperature difference between the inner and outer copper blocks. When measuring the temperature of the solution, thermoelement D_{24} is connected in series with the main working thermoelement, W_{24}, so that the outer block temperature cancels and the temperature of the inner block becomes the reference for measuring the solution temperature. In Figures 2 and 3 the thermoelements are shown as single junctions to avoid confusion. The junctions are grouped and inserted in holes in the blocks. In operation, the temperatures of the two blocks were equalized by means of their resistance heaters. The temperature of bath *F* was adjusted to the same temperature and maintained at this temperature by means of thermoregulator *I* and heater *K*. The bath was stirred vigorously by stirrer *L*. The temperature of the thermostat was automatically maintained constant within ±0.010° F. *H* is an auxiliary cooling coil.

At 131° F. and with the thermostat adjusted so that the difference between the two blocks remained zero as indicated by thermoelement D_{24} over a 3-hour period, the actual temperature of the blocks as indicated by thermoelement C_4 was observed at frequent intervals and found to increase linearly with time at a rate of 0.0003° F. per minute. The rate of increase was greater at higher temperatures. It is possible that chemical action caused the drift since the copper blocks were covered with a light film of oil. No error was introduced in the measurements of temperature changes of the solutions by this linear drift, since it is eliminated in the same manner as the drift due to stirring.

Solutions

Thermoprene-lined (*12*) glass, nickel, or monel metal vessels were used in preparing the solutions. Stock solutions were made by first preparing crystalline $NaOH \cdot H_2O$ from C. P. stick sodium hydroxide and redissolving the solid to produce a saturated solution at room temperature. The insoluble sodium carbonate was removed by settling. The solutions were analyzed gravimetrically with an accuracy of ±0.005 per cent by the method suggested by Richards and Hall (*9*).

Heat Capacity of Calorimeter

The heat capacity of the calorimeter was determined electrically, using water, in a manner identical to that used in measuring the heat capacities of the solutions. Measurements were made in a range from 40° to 140° F. At 68° F. the heat capacity was also calculated from the heat capacities and weights of the constituent parts, and the value obtained agreed within 0.7 per cent with that found by direct measurement.

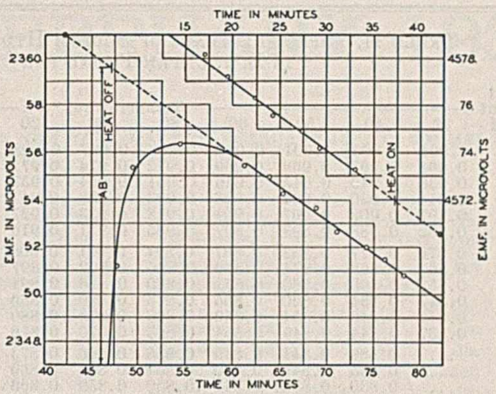

FIGURE 4. TEMPERATURE DRIFTS IN A TYPICAL RUN

Method of Operation

From the foregoing much of the experimental procedure may be inferred. With a solution of given concentration, several specific heat determinations were made at different temperatures. The cold calorimeter was first brought to equilibrium at a temperature about midway in the range to be covered. In order to correct for the heat of stirring and for the small temperature drift of the cold calorimeter, each experiment consisted of three periods: a fore period, a heating period, and an afterdrift period. Readings of time and e. m. f. of thermoelement $W_{24} + D_{24}$ were made at intervals for at least 15 minutes before starting the heating current and for at

TABLE I. SUMMARY OF HEAT CAPACITY RUNS

NaOH *Weight %*	Temp. *° F.*	Heat Capacity *B. t. u./lb./° F.*
4.081	37.62	0.9380
	46.89	0.9416
	68.00	0.9476
	86.00	0.9523
6.920	39.49	0.9113
	44.89	0.9141
	55.89	0.9184
	76.95	0.9254
21.38	42.73	0.8465
	43.12	0.8473
	50.36	0.8506
	51.66	0.8520
	61.77	0.8566
	69.04	0.8590
	77.31	0.8623
	86.36	0.8666
29.71	46.54	0.8286
	58.21	0.8344
37.53	42.21	0.8150
	49.73	0.8172
	58.55	0.8208
50.88	55.98	0.7685
	68.22	0.7670
	77.90	0.7661
	93.02	0.7651
6.80	67.82	0.9230
7.39	67.69	0.9179
	69.48	0.9184
8.91	67.91	0.9070
17.70	68.47	0.8695
	78.87	0.8731
20.98	68.47	0.8607
	77.11	0.8645
	86.00	0.8683
31.52	68.32	0.8372
	77.40	0.8413
	86.40	0.8451
37.10	67.95	0.8248
	77.38	0.8286
40.44	68.29	0.8153
	77.02	0.8179
	86.04	0.8198
41.48	68.11	0.8126
	77.02	0.8143
	86.27	0.8148
47.71	68.11	0.7857
	76.75	0.7840
	86.11	0.7849
5.78	106.18	0.9406
	122.50	0.9428
	140.09	0.9454
	154.27	0.9476
11.90	103.80	0.9027
	124.20	0.9046
	139.23	0.9089
	154.67	0.9108
19.89	107.10	0.8776
	120.47	0.8802
	140.49	0.8840
	158.38	0.8857
29.53	103.78	0.8580
	122.41	0.8633
	140.11	0.8676
	155.41	0.8688
39.44	103.05	0.8286
	105.75	0.8294
	121.96	0.8320
	140.14	0.8337
	156.11	0.8348
About 44% not analyzed	81.59	0.8036
	103.48	0.8052
	122.18	0.8057
51.15	122.22	0.7606
	140.04	0.7596
	155.77	0.7587
45.20	142.32	0.7997
	157.37	0.7981
	176.27	0.7971
48.70	150.67	0.7744
	176.32	0.7728
	191.37	0.7723

TABLE II. SPECIFIC HEATS OF SODIUM HYDROXIDE SOLUTIONS IN B. T. U. PER POUND PER ° F.

Weight Per Cent NaOH	Temperature, ° F.: 32	40	50	60	80	100	120	140	160	180	200
0	1.004	1.003	1.001	0.999	0.998	0.997	0.998	0.999	1.000	1.002	1.004
2	0.965	0.967	0.968	0.969	0.972	0.974	0.977	0.978	0.980	0.983	0.986
4	0.936	0.940	0.943	0.946	0.951	0.954	0.957	0.960	0.962	0.965	0.966
6	0.914	0.920	0.924	0.928	0.933	0.938	0.941	0.944	0.946	0.948	0.950
8	0.897	0.902	0.907	0.911	0.918	0.923	0.927	0.930	0.932	0.934	0.936
10	0.882	0.888	0.893	0.897	0.905	0.911	0.916	0.918	0.920	0.922	0.923
12	0.870	0.877	0.883	0.887	0.894	0.901	0.906	0.909	0.911	0.912	0.913
14	0.861	0.868	0.874	0.879	0.886	0.892	0.897	0.901	0.903	0.903	0.904
16	0.853	0.860	0.866	0.871	0.880	0.886	0.891	0.894	0.896	0.897	0.897
18	0.847	0.854	0.860	0.865	0.873	0.880	0.885	0.888	0.890	0.891	0.891
20	0.842	0.848	0.854	0.859	0.868	0.875	0.880	0.884	0.886	0.886	0.887
22	0.837	0.844	0.849	0.854	0.863	0.870	0.876	0.880	0.882	0.882	0.883
24	...	0.839	0.844	0.849	0.858	0.866	0.873	0.877	0.879	0.879	0.880
26	...	0.835	0.840	0.845	0.854	0.863	0.869	0.874	0.875	0.876	0.876
28	...	0.830	0.836	0.841	0.850	0.859	0.866	0.870	0.872	0.872	0.873
30	...	0.826	0.832	0.837	0.846	0.855	0.862	0.866	0.868	0.869	0.869
32	...	0.822	0.828	0.833	0.842	0.850	0.857	0.862	0.863	0.864	0.864
34	...	...	0.823	0.828	0.837	0.845	0.852	0.856	0.857	0.858	0.858
36	...	...	0.819	0.824	0.832	0.840	0.845	0.849	0.850	0.851	0.851
38	...	...	0.816	0.820	0.827	0.833	0.837	0.841	0.842	0.842	0.843
40	...	...	0.812	0.815	0.821	0.826	0.829	0.831	0.832	0.832	0.832
42	...	...	0.807	0.809	0.813	0.816	0.819	0.819	0.820	0.820	0.820
44	...	...	...	0.802	0.804	0.806	0.807	0.807	0.807	0.806	0.804
46	...	...	...	0.793	0.794	0.795	0.794	0.794	0.793	0.791	0.789
48	...	...	...	...	0.783	0.782	0.781	0.780	0.779	0.777	0.776
50	...	...	...	...	0.771	0.769	0.768	0.767	0.765	0.765	0.764
52	...	...	...	...	0.758	0.756	0.755	0.754	0.753	0.752	0.752

least 20 minutes after stopping the current. On plotting these points and extrapolating the nearly parallel lines so obtained to the middle of the heating period, the difference in e. m. f. values at this point gave the true change in e. m. f. due to the electrical energy input. The trend of the afterdrift immediately after stopping the heating current indicated that the temperature of the metal parts of the calorimeter lagged perhaps 0.04° to 0.05° F. behind that of the solution. Figure 4 shows the e. m. f. *vs.* time curves for a typical run in which the heating was started at time 37 minutes and stopped at time 47 minutes. The decreasing values of e. m. f. with time were due to the fact that the cold junctions of thermoelement $W_{24} + D_{24}$ were at a higher temperature than those in the solution. As may be seen from Figure 4, the temperature of the solution in the region of thermoelement W_{24} decreased slightly immediately after stopping the heating current. The distance *AB* represents a temperature difference of approximately 0.02° F., and this temperature change is accounted for by the equalization of temperature after the heating current was turned off.

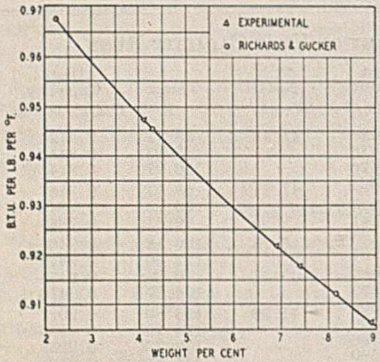

FIGURE 5. HEAT CAPACITIES AT 20° C.

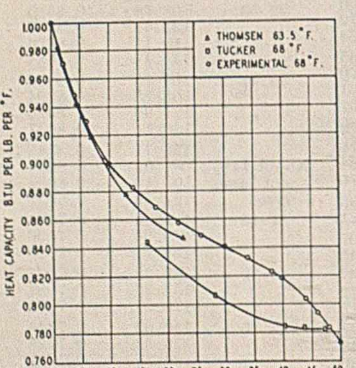

FIGURE 6. COMPARISON OF SPECIFIC HEAT DATA

Eighty per cent of the calculated evaporation correction was applied to measurements in which evaporation inside of vessel *A* was appreciable, although the correction was in any case very small.

Results of Measurements

The results of eighty-one measurements are shown in Table I. Few measurements were made above 158° F., but it was found that above 140° F. the heat capacities were practically independent of temperature so that little uncertainty was involved in extrapolating to higher temperatures. The temperature coefficient of the heat capacity near 32° F. is of considerable magnitude and changes rapidly with temperature so that extrapolation to 32° F. was comparatively unsatisfactory. The heat capacities were converted to B. t. u. per pound per ° F., were cross-plotted on a large scale, and were rounded to even values of concentration and temperature. The results are given in Table II. The conversion factor used was 4.1876 joules per gram calorie.

Comparison with Previous Work

Figure 5 shows a comparison of the heat capacity values of Richards and Gucker (*8*) at 68° F. with those of the present work at the same temperature. The agreement is well within the probable precision of the measurements.

A similar comparison was made with the specific heats measured by Gucker and Schminke (*3*) at 77° F. The maximum difference found was 0.13 per cent at a concentration of 4 per cent.

In Figure 6 are plotted the specific heat data of Tucker (*14*) at a mean temperature of 68° F., of Thomsen (*13*) at a mean temperature of 63.5° F., and those of the present work at 68° F. Thomsen's values would be increased slightly if corrected to 68° F., so his work is in good agreement. Tucker's data, over a considerable concentration range, lie on a curve almost parallel with, but considerable lower than, that of the present work. Apparently an almost constant error entered into his results.

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MARKET REPORT—FEBRUARY, 1936

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, FEBRUARY 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Acetaldehyde, drums, lc-l., wks	lb.	.16
Acetaldol, 50-gal. drums	lb.	.27
Acetamide, drums	lb.	.38
Acetanilide, U. S. P., powd., bbls.	lb.	.26
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks., c/l.	lb.	.12
Acetphenetidin, bbls.	lb.	1.30
Acid, abietic	lb.	.07
Acetic, 28%, c/l., bbls.	100 lbs.	2.45
56%, c/l., bbls.	100 lbs.	4.75
Glacial, c/l., drums	100 lbs.	8.43
Glacial, U. S. P., c/l., carboys	100 lbs.	11.00
Acetylsalicylic, bbls.	lb.	.70
Adipic	lb.	.72
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, tech., bbls.	ton	95.00
Butyric, 100% basis, cbys.	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.03½
Chromic, 99%, drums	lb.	.14¾
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.28
Cresylic, pale, drums	gal.	.68
Formic, 90%, cbys., N. Y.	lb.	.11
Furoic, tech., drums	lb.	.35
Gallic, U. S. P., bbls.	lb.	.77
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.07
60%, bbls., wks.	lb.	.15
Hydrofluosilic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.75
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11½
Linoleic, drums	lb.	.16
Maleic, kegs	lb.	.29
Mixed, tanks, wks.	N unit	.07
	S unit	.008
Molybdic, 85%, kegs	lb.	1.25
Naphthenic, drums	lb.	.14
Naphthionic, tech., bbls.	lb.	nom.
Nitric, c. p., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11⅛
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.60
Salicylic, tech., bbls.	lb.	.33
Sebacic, tech., drums	lb.	.58
Stearic, d. p., bbls., c/l.	lb.	.10
Sulfanilic, 250-lb. bbls.	lb.	.18
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Tannic, tech., bbls.	lb.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.25
Tungstic, kegs	lb.	1.35
Valeric, c. p., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	4.485
Amyl, from pentane, tanks	lb.	.143
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.12
Capryl, pure, for perfume	lb.	24.00
Cinnamic	lb.	3.50
Denatured, No. 5, comp. denat., c/l., drums	gal.	.44
Furfuryl, tech., 500-lb. drums	lb.	.35
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	.11½
Isopropyl, ref., drums	gal.	.45
Propyl, ref., drums	gal.	.75
Wood, *see* Methanol		
Aldol, 95%, drums, c/l.	lb.	.21
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.33
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.00
Chrome, casks, wks.	100 lbs.	7.00
Potash, lump, bbls., wks.	100 lbs.	3.00
Soda, bbls., wks.	100 lbs.	4.00
Aluminum, metal, N. Y.	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.18
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.35
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks.	lb.	.04½
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.15¼
Bromide, bbls.	lb.	.39
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.50
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	3.40
Linoleate, drums	lb.	.12
Nitrate, tech., cryst., bbls.	lb.	.08½
Oleate, drums	lb.	.10
Oxalate, kegs	lb.	.24
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls.	lb.	.08½
Sulfate, bulk, wks.	ton	22.00
Amylene, tanks, wks.	lb.	.09
Amyl acetate, tech., from pentane, tanks, delivered	lb.	.135
Amyl chloride, normal, drums, wks.	lb.	.56
Amyl chlorides, mixed, tanks, wks.	lb.	.06
Amyl mercaptan, drums, wks.	lb.	1.10
Aniline oil, drums	lb.	.16½
Anthracene, 80–85%, casks, wks.	lb.	.75
Anthraquinone, subl., bbls.	lb.	.50
Antimony, metal	lb.	.12⅝
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.13½
Salt, dom., bbls.	lb.	.22
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.22
Argols, red powder, bbls.	lb.	.07
Arsenic, metal, kegs	lb.	.44
Red, kegs, cases	lb.	.15¾
White, c/l., kegs	lb.	.04½
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	45.00
Chloride, bbls., wks.	ton	74.00
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05
Nitrate, casks	lb.	.08½
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzidine base, bbls.	lb.	.72
Benzine, tanks, wks.	gal.	.18
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.60
Alcohol, drums	lb.	.75
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	1.00
Bismuth, nitrate, 25-lb. jars	lb.	1.10
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.30
Blanc fixe, dry, bbls.	ton	65.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	ton	40.00
Bordeaux mixture, bbls.	lb.	.10½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.75
Butyl acetyl ricinoleate, drums	lb.	.24
Acetate, drums, c/l.	lb.	.12
Aldehyde, drums	lb.	.18
Carbinol, norm., drums, wks.	lb.	.60
Carbinol, sec., wks.	lb.	.60
Lactate, drums	lb.	.22½
Oleate, drums	lb.	.25
Stearate, drums	lb.	.25
Cadmium, metal, cases	lb.	.65
Cadmium bromide, 50-lb. jars	lb.	1.54
Cadmium sulfide, boxes	lb.	1.00
Caffeine, U. S. P., 5-lb. cans	lb.	1.85
Calcium acetate, bags	100 lbs.	2.10
Arsenate, bbls.	lb.	.06½
Carbide, drums	lb.	.05½
Carbonate, U. S. P., precip., 175-lb. bbls.	lb.	.06½
Chloride, bags, wks., flake	ton	19.50
Cyanide, 100-lb. drums	lb.	.30
Gluconate, U. S. P.	lb.	.57
Tech.	lb.	.28
Nitrate, bags, 15% N	ton	25.50
Phosphate, monobas., bbls.	lb.	.07½
Tribas., bbls.	lb.	.11
Camphor, Jap., slabs	lb.	.55
Carbazole, bbls.	lb.	.80
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.051
Carbon black	lb.	.04†
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.05¼
Casein, stand. gr., bbls.	lb.	.15
Cellulose acetate, bbls.	lb.	.80
Cerium oxalate, kegs	lb.	.25
Charcoal, willow, powd., bbls.	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq. c/l., cyl.*	lb.	.055
Chlorine, tanks	100 lbs.	2.15
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks.	bbl.	8.50
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	1.39
Copperas, c/l., bulk	ton	14.00
Copper, metal, elec.	100 lbs.	9.50
Copper carbonate, bbls., 52/54%	lb.	.15½
Chloride, bbls.	lb.	.17
Cyanide, drums	lb.	.37
Oxide, red, bbls.	lb.	.15
Sulfate, c/l., bbls.	100 lbs.	3.85
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.16¾
Crotonaldehyde, 50-gal. drums, c/l.	lb.	.26
Cyanamide, bulk, N. Y.	Ammonia unit	1.07½
Diaminophenol, kegs	lb.	3.80
Diamylamine, drums, wks.	lb.	1.00
Diamylene, tanks, wks.	lb.	.08½
Diamyl ether, drums, wks.	lb.	.09
Diamyl sulfide, drums, wks.	lb.	1.10
Diamyl phthalate, tanks	lb.	.18

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† This is the approximate F. O. B. shipping point price. Quotations are now all on a delivered basis and vary with the section.

* F. O. B. destination.

Dianisidine, bbls.	lb.	2.35
Dibutoxyethyl phthalate, wks., drums	lb.	.42
Dibutyl ether, drums	lb.	.30
Dibutylphthalate, drums, wks.	lb.	.20
Dibutyl tartrate, drums	lb.	.35
Dichlorethyl ether, 50-gal. drums, c/l.	lb.	.21
Dichloropentanes, tanks, wks.	lb.	.02½
Diethanolamine, drums	lb.	.31
Diethylaniline, drums	lb.	.52
Diethylene glycol, drums	lb.	.15½
Monobutyl ether, drums	lb.	.26
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.26
Diethyl carbinol, drums, wks.	lb.	.60
Diethyl phthalate, drums	lb.	.18½
Diethyl sulfate, tech., drums	lb.	.20
Diglycol oleate, drums	lb.	.24
Dimethylamine, pure 25.40% sol.—100% basis, drums	lb.	.95
Dimethylaniline, drums	lb.	.29
Dimethyl ethyl carbinol, drums, wks.	lb.	.60
Dimethylsulfate, drums	lb.	.45
Dimethyl phthalate, drums	lb.	.20
Dinitrobenzene, tech., drums	lb.	.17
Dinitrochlorobenzene, bbls.	lb.	.14½
Dinitronaphthalene, bbls.	lb.	.34
Dinitrophenol, bbls.	lb.	.23
Diphenyl	lb.	.15
Diphenylamine, bbls.	lb.	.31
Diphenylguanidine, bbls.	lb.	.36
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.80
Ether, conc., drums	lb.	.09
Ether, nitrous, bot.	lb.	.75
Ethyl acetate, tanks, c/l.	lb.	.07½
Acetoacetate, 110-gal. drums	lb.	.37
Bromide, drums	lb.	.50
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorcarbonate, carboys	lb.	.30
Chloride, drums	lb.	.22
Ether, absolute, 50-gal. drums	lb.	.50
Furorate, 1-lb. tins	lb.	5.00
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene dichloride, 50-gal. drums	lb.	.05½
Ethylenechlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.17
Monobutyl ether, drums	lb.	.20
Monoethyl ether, drums	lb.	.15
Monoethyl ether acetate, drums	lb.	.16½
Monomethyl ether, drums	lb.	.21
Oxide, cylinders	lb.	.55
Feldspar, bulk	ton	10.00
Ferric chloride, tech., bbls.	lb.	.05
Ferrous chloride, cryst., bbls.	lb.	.06
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls.	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	6.50
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls.	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, c. p., drums	lb.	.14½
Glyceryl phthalate, drums	lb.	.28
Glycol phthalate, drums	lb.	.29
Stearate, drums	lb.	.23
G salt, bbls.	lb.	.45
Hexamethylenetetramine, tech., drums	lb.	.37
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20% paste, bbls.	lb.	.12
Iodine, resubl., jars	lb.	1.65
Iron acetate, liq., 17°, bbls., c/l.	lb.	.03
Isobutyl carbinol (128–132° C.), tanks	lb.	.32
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y.	100 lbs.	4.50
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls.	lb.	.08
Oxide, litharge, bbls., 20-ton lots	lb.	.06
Peroxide, drums	lb.	.20
Red, bbls., 20-ton lots	lb.	.07
Sulfate, bbls.	lb.	.06
White, basic carb., bbls.	lb.	.06½
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	280 lbs.	1.70
Limestone, ground, bags, wks.	ton	4.50
Lithopone, bbls.	lb.	.04½
Magnesite, calcined, 500-lb. bbls., wks.	ton	60.00
Magnesium, metal, wks.	lb.	.30
Magnesium carbonate, bags	lb.	.06½
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 100 lbs.	lb.	.81
Mercury flasks, 76 lbs.	flask	77.00
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, bbls.	lb.	.82
Meta-tolylenediamine, bbls.	lb.	.67
Methanol, pure, synthetic, drums, delivered, c/l.	gal.	.37½
Tanks, delivered	gal.	.35½
Methyl acetone, tanks	gal.	.44
Methyl chloride, cylinders	lb.	.45
Hexyl ketone, pure	lb.	1.20
Methyl propyl carbinol, drums, wks.	lb.	.60
Methyl salicylate, cases	lb.	.42
Michler's ketone, bbls.	lb.	2.50
Monoamylamine, drums, wks.	lb.	1.00
Monoethanolamine, drums	lb.	.31
Monomethylamine, drums	lb.	.75
Naphthalene, flake, bbls.	lb.	.06¼
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.13
Double, bbls.	lb.	.13
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.09
Octyl acetate, tanks	lb.	.15
Oil, castor, No. 1	lb.	.10¾
China wood, bbls.	lb.	.14⅜
Coconut, tanks	lb.	.04⅝
Cod, N. F., bbls.	gal.	.40
Corn, crude, tanks, mills	lb.	.09½
Cottonseed, oil refined, tanks	lb.	.10½
Linseed, boiled, bbls.	lb.	.104
Menhaden, crude, tanks	gal.	.36
Neat's-foot, pure, bbls.	lb.	.12¾
Oleo, No. 1, bbls.	lb.	.12½
Olive oil, denat., bbls.	gal.	.76
Foots, bbls.	lb.	.08¼
Peanut, crude, tanks	lb.	.08¾
Perilla, bbls.	lb.	.07
Rapeseed, bbls.	gal.	.54
Red, bbls.	lb.	.09⅝
Soy bean, crude, tanks	lb.	.09
Sperm, 38°, bbls.	lb.	.099
Whale, bbls., natural, refined	lb.	.075
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.07
Ortho-toluidine, bbls.	lb.	.14
Paraldehyde, 110–50-gal. drums	lb.	.16
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.16
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.47
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls.	lb.	.45
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.35
Para-phenylenediamine, bbls.	lb.	1.15
Para-tertiary amyl phenol, drums, wks.	lb.	.50
Para-toluidine, bbls.	lb.	.56
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.60
Phenylethyl alcohol, 1-lb. bot.	lb.	3.75
Phloroglucinol, tech., drums	lb.	15.00
c. p., drums	lb.	20.00
Phosphorus, red, cases	lb.	.45
Oxychloride, 175-lb. cylinders	lb.	.20
Trichloride, cyl.	lb.	.18
Phthalic anhydride, bbls.	lb.	.14½
Platinum, metal, solid	oz.	36.00
Potash, caustic, drums	lb.	.06¼
Potassium abietate	lb.	.06
Acetate, kegs	lb.	.27
Bicarbonate, casks	lb.	.07½
Bichromate, casks	lb.	.08½
Binoxalate, bbls.	lb.	.14
Bromide	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.06
Chlorate, kegs	lb.	.09
Chloride, crystals, bbls.	lb.	.04¾
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.13½
Muriate, fert., bulk, per K_2O unit		.40
Permanganate, drums	lb.	.18½
Prussiate, red, casks	lb.	.35
Yellow, casks	lb.	.18
Titanium oxalate, bbls.	lb.	.32
Pyridine, drums	gal.	1.30
Pyrocatechin, c. p., drums	lb.	2.40
Resorcinol, tech., kegs	lb.	.75
Rochelle salt, bbls., U. S. P.	lb.	.14
R salt, bbls.	lb.	.52
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	13.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.32⅝
Soda, ash, 58%, light, bags, contract, wks.	100 lbs.	1.23
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.60
Sodium abietate, drums	lb.	.06
Acetate, bbls.	lb.	.05
Alginate, drums	lb.	.64
Benzoate, bbls.	lb.	.46
Bicarbonate, bbls.	100 lbs.	1.85
Bichromate, casks	lb.	.06½
Bisulfite, bbls.	lb.	.03
Bromide, bbls., U. S. P.	lb.	.35
Chlorate, kegs	lb.	.05
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls.	lb.	.07½
Metallic, drums, 12¼-lb. bricks	lb.	.19
Metasilicate, cryst.	100 lbs.	3.25
Metasilicate, gran., bbls.	100 lbs.	2.65
Naphthenate, drums	lb.	.13
Naphthionate, bbls.	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y.	ton	24.80
Nitrite, bbls.	lb.	.07¼
Perborate, bbls.	lb.	.17
Peroxide, cases	lb.	.20
Phosphate, disodium, bags	100 lbs.	2.10
Phosphate, trisodium, bbls.	100 lbs.	2.30
Picramate, kegs	lb.	.67
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls.	lb.	.05¼
Stannate, drums	lb.	.32
Sulfate, anhyd., bbls.	100 lbs.	1.30
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.30
Thiosulfate, reg., cryst., bbls.	lb.	.02½
Tungstate, kegs	lb.	.85
Strontium carbonate, tech., bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.08¾
Peroxide, 100-lb. drums	lb.	1.25
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Tetrachlorethane, 50-gal. drums	lb.	.08½
Thiocarbanilid, bbls.	lb.	.25
Tin	lb.	.47¾
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.24¾
Oxide, bbls.	lb.	.51
Titanium dioxide, bbls., wks.	lb.	.17¼
Toluene, tanks	gal.	.30
Triamylamine, drums, wks.	lb.	1.25
Tribromophenol, cases	lb.	1.10
Trichloroethylene, 50-gal. drums	lb.	.09½
Triethanolamine, 50-gal. drums	lb.	.26
Trihydroxyethylamine oleate, drums	lb.	.40
Stearate	lb.	.35
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls.	lb.	.37
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.15
Vinyl chloride, 16-lb. cylinders	lb.	1.00
Whiting, bags	ton	7.00
Xylene, 10°, tanks, wks.	gal.	.30
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	4.85
Zinc ammonium chloride, bbls.	lb.	.0465
Chloride, granulated, drums	lb.	.05
Oxide, Amer., bbls.	lb.	.05
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25
Stearate, bbls.	lb.	.20
Zinc dust, bbls., c/l.	lb.	.065